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Effects of Conservation Reserve Program on Runoff and Lake Water Quality in an Oxbow Lake Watershed

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Abstract: A case study of Beasley Lake Watershed, located in the Mississippi Delta region of the U.S., was used to evaluate runoff from edge-of-field sites under either row crop management practices or planted in trees under the Conservation Reserve Program (CRP). Beasley Lake Watershed, with a history of long-term ARS natural resource research, was selected as one of fourteen watersheds for participation in the Conservation Effects Assessment Program (CEAP), a nationwide assessment by USDA-Agriculture Research Service (ARS) and USDA-Natural Resources Conservation Service (NRCS) regarding the effectiveness of USDA conservation programs. Approximately one-third of the Beasley Lake watershed (ca. 280 ha) was converted from cropped land to CRP beginning in 2003, and the remainder of the cropland is managed for soybean, cotton, or corn production. Sub-drainage areas (1.2 to 6 ha) with similar topography and soil types were either cropped (three reduced tillage sites) or placed in CRP (three CRP sites) and were instrumented in 2005 to collect water samples from field drainage slotted-inlet pipes during all surface runoff events. Runoff samples were analyzed for sediments and nutrients. This paper reports on runoff, sediment, and nutrient losses from each sub-drainage area. Establishing trees within areas adjacent to the oxbow lake reduced the total sediments by 85% and nutrients by greater than 28% leaving the watershed as compared to reduced-till crop management techniques. The impact of converting the cropped area into trees has reduced the sediment load entering the lake by an order of magnitude resulting in improved water quality in Beasley Lake based on reductions in nutrient and sediment losses and increases in water visibility.

Keywords: Runoff, Sediment Yield, Water Quality, Conservation Reserve Program (CRP), Reduced-Till.

Introduction

Soil erosion has long been recognized as a threat to the productivity of U.S. farms and the quality of surface waters. Excessive amounts of sediment cause taste and odor problems for drinking water, block water supply intakes, foul treatment systems, and fill reservoirs. A high level of sediment adversely impacts aquatic life, reduces water clarity, and affects recreation. Even in relatively flat areas, such as the Mississippi Delta, considerable soil erosion can occur. Murphree and Mutchler (1981) reported a 5-year average sediment yield as high as 17.7 t ha⁻¹ from a flat watershed in the Mississippi Delta. Cooper and Knight (1990) found that suspended sediment loads generally exceeded 80 to 100 mg L⁻¹ (maximum for optimal fish growth) during and immediately following storm events in two upland streams in Mississippi. Ritchie et al. (1979) found that 2.5 to 7.5 cm of fine sediments accumulated per year in natural lakes along Bear Creek, a drainage system in the Mississippi Delta where 75% of the land was in cultivation. Accumulated sediment has covered the bottoms of many lakes and stream sections with fine silt (Ritchie et al., 1986).

Fertilizers are extensively used in the United States to increase crop production. The wide spread use of fertilizer continues to be a major public concern because of possible human health risks and the eutrophication of surface water (Novotny & Olem, 1994). Nitrate concentration is a parameter of particular concern because of its link to the “blue baby” syndrome and formation of carcinogenic compounds.

Improvement of water resources has been an issue of significant societal and environmental concern for many years. Off-site transport of sediment and its associated pollutants from agricultural
cropland has been classified as one of the major sources of water quality impairment, and water quality would directly benefit if the amount of soil loss was reduced (Natural Resource Conservation Service, 1997). Impairment to surface water quality due to sediment and nutrient transport from agricultural cropland has been estimated to be about $9 billion per year (Ribaudo, 1992). Although more than $500 billion has been spent on water pollution control since the implementation of the Clean Water Act in 1972, the quality of the U.S. water still remains largely unknown (Akobundu & Riggs, 2000). Also, the Mississippi River system has been cited as a leading contributor to conveying sediments and other pollutants into the Gulf of Mexico resulting in hypoxia issues (Scavia, et al. 2003).

In reducing soil erosion and solving nonpoint source (NPS) water quality problems, regulatory agencies promote Best Management Practices (BMPs), as defined by Natural Resources Conservation Service, adoption on areas most susceptible to NPS pollution. Under the USDA Environment Quality Incentive Program (EQIP), cost sharing is available from government agencies to agricultural producers who voluntarily implement BMPs (Natural Resource Conservation Service, 2001). Depending on local priorities and funding availability, the cost-sharing rate is up to 50 percent and may be more. Therefore, a significant amount of research has been conducted to identify management options for minimizing sediment yield and NPS pollution from agricultural land areas. Examples of such management options include conservational tillage (Loehr et al., 1979; Mueller et al., 1984), grass filter strips (Dillaha et al., 1989; Line, 1991; Cooper and Lipe, 1992; Robinson et al., 1996), and impoundments that retard flow and allow suspended sediment transported in runoff sufficient time to drop out of suspension (Laflen et al., 1978). However, the impact of a particular BMP on water quality is still a challenge to estimate before any actual implementation (Parker et al., 1994; Walker, 1994) at a particular location since data from one location may not be applicable to other locations. It is even more difficult to predict integrated effects of implementation of several BMPs.

Various national initiatives and programs have focused on assessing the impact agricultural BMPs have on water conservation and quality over the past two decades. The 1989 Presidential Initiative on Water Quality established water quality objectives and a framework for a national research and assessment endeavor called the Management Systems Evaluation Areas (MSEA) as part of the United States Department of Agriculture Water Quality Program (USDA, 1994). The multi-agency National MSEA program initially focused on five Midwestern states and then expanded to other areas, including Mississippi (Locke, 2004). The Mississippi MSEA (MD-MSEA) project was located in the Mississippi Delta (Figure 1) and was comprised of three oxbow lake watersheds, including Beasley Lake Watershed.

Changes in US farm policy redirected USDA conservation programs to address natural resource issues such as water quality and ecosystem protection as high priorities. This commitment to environmental stewardship extended to the 2002 Farm Bill, with significant increases in funding for conservation programs. The USDA-Agriculture Research Service (ARS) partnered with USDA-Natural Resources Conservation Service (NRCS) in a nationwide assessment regarding the effectiveness of USDA conservation programs that was termed the Conservation Effects Assessment Program (CEAP). Fourteen watersheds, including Beasley Lake Watershed, with a history of long-term ARS natural resource research were selected as benchmark locations for participation in CEAP. A significant database from Beasley Lake Watershed spanning from 1994 to 2003 (MD-MSEA research) and into the present (CEAP) serves as an important tool for supporting CEAP goals (Locke et al., 2008).

As part of the CEAP assessments, this paper reports and compares the runoff and water quality from 2005 to 2008 from edge-of-field drainage sites with row crop management practices to drainage sites with Conservation Reserve Program (CRP). Also, this paper assesses the water quality of the lake by analyzing lake water samples for sediments and nutrients.

**Materials and Method**

A case study of Beasley Lake Watershed, typical of topography and cropping systems in the Mississippi Delta region, was used to evaluate water quality from various BMPs placed throughout the watershed. The Mississippi Delta region (Figure 1) comprises 11 million hectares of the southern portion of the Mississippi River Alluvial Plain.
Figure 1. Map of area of United States that represents a sub region of the Lower Mississippi River Basin, an alluvial plain known as the Mississippi Delta.

This alluvial plain region is a narrow strip on both sides of the Mississippi River, widening in some places to approximately 160 kilometers, that extends over 1100 kilometers from southeastern Missouri to the Gulf of Mexico. Historically, cotton (Gossypium hirsutum L.) production dominated the rural and intensively agricultural region, but in recent decades, agriculture has diversified to soybeans [Glycine max (L.) Merr.], rice (Oryza sativa), catfish (Ictalurus punctatus), and corn (Zea mays L.). The climate is classified as humid subtropical with an annual rainfall ranging from 1140 to 1520 mm and temperatures averaging 18°C. Although the Delta region topography averages less than 1% slope, significant quantities of sediment are lost in runoff from the high rainfall events common during winter and spring months.

Beasley Lake Watershed (latitude 33°24′15″, longitude 90°40′05″) is located in Sunflower County, Mississippi, and part of the Big Sunflower River watershed (hydrologic unit code 08030207) within the Yazoo River Basin (Locke, et al., 2008). Beasley Lake (Figure 2) is a 25-ha oxbow lake resulting from a course shift by the nearby Sunflower River. The total drainage area of this watershed is approximately 850 ha. The Sunflower River levee defines the northern part of the watershed boundary. Soils are generally loam to heavy clay, with part of the watershed being forested. Further watershed details, description of soil survey, data and management decisions with respect to time can be found in Locke, et al., 2008. Drainage of the watershed is dependent on man-made ditches with water draining into Beasley Lake. The predominant watershed crop is soybean, but corn and cotton are rotationally grown.

Beasley Lake Watershed has evolved from row crop agriculture dominated by cotton production to a mixture of row crop and non-cropped areas from 1995 through 2008 (Figure 3). Approximately 12% (113 ha) of the Beasley Lake Watershed was converted from cropped land to CRP beginning in 2003, and the remainder of the cropland was still managed for soybean, cotton, or corn production. Beginning in 2005, research was initiated involving monitoring runoff from edge of field slotted-inlet drainage pipe sites on both CRP and cropped land. Six sub-drainage areas (1.2 to 6 ha) (denoted by green squares in Figure 2) of similar topography and soil types were selected from areas either cropped in reduced tillage soybean (three sites) or planted in eastern cottonwood (Populus deltoids), oak (Quercus sp.) and hickory (Carya sp.) trees and set aside as Conservation Reserve (CRP) (three sites). These trees, planted on a 2 m by 2 m grid, are some of the largest North American hardwood trees and are grown in riparian areas. Global positioning system (GPS) surveys were used to establish/delineate drainage acreages (4-6 ha) for each site.
Bermed borders were created to delineate sub-drainage areas for measuring surface runoff. Rain and runoff from rain events producing runoff were measured and sampled. Rain was measured using 1-mm tipping buckets connected to area-velocity flow logger/meters within the study area (denoted in Figure 2 by black triangles). Runoff was determined from flow measurements using area-velocity flow logger/meters and acoustic Doppler devices mounted in slotted-inlet pipes positioned at the outlets of the sub-drainage areas. Runoff from these rain events was collected starting in April 2005 from these sub-drainage areas instrumented with these relatively simple and compact area-velocity flow logger/meters and automated composite water samplers. Water samplers automatically collected runoff samples from field drainage slotted-inlet pipes on a flow proportional basis via acoustic Doppler technique during all surface runoff events. Within 24 h of rainfall events, runoff samples were collected, transported to the National Sedimentation Laboratory in Oxford, MS, and stored at 4°C (usually <24 h) for analysis. Runoff, sediment yield or soil loss, and nutrient loss were determined for each site. Water samples were filtered through 0.45 μm nitrocellulose membranes to produce the filterable and nonfilterable nutrient components of total kjeldahl nitrogen (TKN) and total phosphorus (TP). Analytical and chemical methods were based on procedures from APHA (1992). Calculation of means and statistical analysis were completed using SAS STAT software (SAS Institute, Inc., 2006).

Three lake water sampling sites (denoted by yellow dots in Figure 2) were selected for water quality monitoring with locations at one-third distance from inlet, mid-point of lake, and one-third distance from outlet. At these locations, water was collected in sample bottles within 5 cm of the lake’s surface on a biweekly basis from May 1995 through December 2008 and analyzed for total, suspended, and dissolved sediments, TP, filterable orthophosphate, ammonium nitrogen and nitrate nitrogen, chlorophyll, coliform and enterococci bacterial counts. A Secchi visibility determination was made at each site by placing a Secchi disc into the water column and measuring the distance to where it initially disappeared. Results from this data from May 1995 to December 1999 are found in Cullum et al. (2006). This paper extends the use of the total, suspended, and dissolved sediments, the Secchi visibility, and some of the chemical data of ammonium nitrogen, nitrate nitrogen, orthophosphate, and total phosphorus to assess the land management effects on the receiving water body.

The hypothesis being tested is that improvement in edge-of-field water quality can be demonstrated via land placed in CRP. Improvement in edge-of-field water quality was primarily based on the reduction of sediments, since many of the contaminants of interest entering water bodies are associated with these particles. Improvement in edge-of-field water quality consists of evaluating differences in sediment and nutrients in runoff resulting from converting cropped land to CRP. Selected fields (three cropped or tillage sites and three CRP sites) in the Beasley watershed were automated to collect surface water samples from field drainage slotted-inlet pipes during all surface runoff events. Runoff samples were analyzed for sediments and nutrients. Both soil and chemical loss
and runoff data were analyzed on a quarterly, annual, and total basis. Statistical analysis was conducted by comparing CRP sites to row crop sites to determine effectiveness of CRP to improve water quality, chiefly by reducing sediments. Data were collected from April 2005 to July 2008.

![Figure 3. Map of Beasley Lake Watershed displaying crop changes to watershed from 1995 through 2008.](image)

**Results and Discussion**

When lake data collection began in 1995, 718 ha of the watershed were cropped with cotton (63.3% of cropped area), corn, and soybeans. Typically, farming practices in the watershed included disking the soil in the fall, preparing the seedbeds just prior to planting, and cultivating during the growing season. During the period from 1995 to 2006, implementation of government sponsored conservation programs resulted in dramatic changes within the Beasley watershed (Figure 3). In 2001 and 2002, reduced-till cotton and soybeans occupied most of the cultivated area, and from 2003 to 2006, reduced-till soybeans were the dominant crop. In 2007 these cultivated areas were rotated out of soybeans into corn. In 2008, all the cropped area of the Beasley watershed was rotated to reduced-till soybeans. In fall 2002, 113 ha were removed from row crop production and planted to hardwood trees under the CRP.
Physical water quality data for the six drainage sites are shown in Table 1. Analysis of variance showed significant differences in the means (p=0.05) between the total average runoff and total soil loss from crop areas as compared to CRP areas over the time of study. Differences in runoff and soil loss means among the four years were found within both the crop areas and CRP areas probably due to the annual rainfall quantity differences during this study. The analysis of variance tests also showed a significant difference in means of the quarterly data with the January through March period producing the most runoff (Figure 4) and soil loss (Figure 5) especially in the crop areas.

**Table 1.** Annual rain, runoff, and sediment yield from crop and CRP sites.

<table>
<thead>
<tr>
<th>Year</th>
<th>Rain (mm)</th>
<th>Runoff (mm)</th>
<th>Sediment Yield (kg/ha)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Crop</td>
<td>CRP</td>
<td>Crop</td>
</tr>
<tr>
<td>2005</td>
<td>298</td>
<td>202</td>
<td>56</td>
</tr>
<tr>
<td>2006</td>
<td>632</td>
<td>219</td>
<td>262</td>
</tr>
<tr>
<td>2007</td>
<td>631</td>
<td>355</td>
<td>130</td>
</tr>
<tr>
<td>2008</td>
<td>487</td>
<td>158</td>
<td>147</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>2048</strong></td>
<td><strong>934</strong></td>
<td><strong>595</strong></td>
</tr>
</tbody>
</table>

![Figure 4. Quarterly rain and runoff from the three row crop sites and the three CRP sites.](image)

Of the total rainfall producing runoff events in the watershed, approximately 45 percent was in runoff from land cultivated in row crops while 29 percent was in runoff from CRP areas. These results are shown in Table 1 when comparing the total runoff of 934 mm and 595 mm from crop and CRP, respectively to the 2048 mm of rain producing runoff over the testing period. Annual soil loss from the crop area was 2.1 t ha$^{-1}$ as compared to the annual soil loss from the CRP area of 0.3 t ha$^{-1}$. Total runoff and total soil loss were 36% and 85% lower from the CRP areas than from the cropped areas. Both areas produced lower annual soil loss than the NRCS tolerance level of 3 t ha$^{-1}$; thus, these two best management practices would be considered appropriate for this agricultural watershed.
Figure 5. Quarterly sediment yield (kg/ha) from the three row crop sites and the three CRP sites.

The annual chemical losses from runoff collected from the six drainage sites are shown in Table 2. Similar to observations made concerning total runoff and sediment loss, loss of chemicals was reduced in CRP areas. The total chemical losses for the study (Table 2) within the CRP areas as compared to the cropped areas were 83%, 71%, 35%, 36%, and 28% for NO₂-N, NO₃-N, NH₄-N, PO₄-P, and TOC, respectively. More of TKN was in the filterable component (fine fraction, including soluble) (F) of the sample than in the TKN non-filterable (NF) component (larger sized constituents) for the CRP areas (Table 2). TKN losses within the filterable component of the runoff were reduced by 45% for the study within the CRP areas as compared to that in the cropped areas. The total phosphorus (TP) losses for the study were 969 gm ha⁻¹ and 628 gm ha⁻¹ for the filterable component of the runoff for cropped areas and CRP areas, respectively, and 712 gm ha⁻¹ and 20 gm ha⁻¹ for the NF fraction of the runoff for cropped areas and CRP areas, respectively. TP losses were reduced by 35% and 97% for the F and NF fractions of runoff, respectively, when comparing the CRP areas to the cropped areas.

The lake data indicated reduction of sediments over time when assessing the sediment data from the surface water samples of the lake and the Secchi visibility measurements. The biweekly data was summarized into monthly means for all three sampling points within the lake. The suspended sediments and Secchi visibility data showed significant differences among the months and among the years as shown in Figure 6. Filterable sediments, which are the fine solids and soluble materials, remained relatively stable over time at around 60 mg L⁻¹. Variation among the suspended sediments was three orders of magnitude from 1071 mg L⁻¹ in April 1996 to 4 mg L⁻¹ in 2008. Secchi visibility was from 4 cm in May 1995 to 83 cm in September 2008. An indirect relationship of declining suspended solids with increasing Secchi visibility was observed (Figure 6).

The sediment data and Secchi visibility data (Table 3) were also presented as annual summaries and further divided into three time steps. The first time step was when the edge-of-field conservation practices were first implemented (but with few in-field conservation row crop practices) from 1995 through 1998. The second time step was when some in-field conservation practices were included and the use of transgenic crops was increased from 1999 thru 2003. The third time step was after CRP practices were implemented in a major portion of the watershed from 2004 through 2008. Lake water samples resulted in over 55% reduction of suspended sediments during the third time step or post-CRP implementation period when comparing the second time step of 112 mg L⁻¹ suspended
sediments from 1999 through 2003 to the third time step of 50 mg L\(^{-1}\) suspended sediments from 2004 through 2008. Also, the average Secchi disc depth visibility increased from 21 cm during the second time step from 1999 through 2003 to 44 cm during the third time step or post-CRP implementation period. These data indicate that reduced sediment runoff due to conservation measures in the watershed was positively impacting the lake water quality.

**Table 2.** Mean annual chemical loads from runoff of row crop and CRP sites.

<table>
<thead>
<tr>
<th>Year</th>
<th>Drainage Type</th>
<th>NO(_2)-N (gm/ha)</th>
<th>NO(_3)-N (gm/ha)</th>
<th>NH(_4)-N (gm/ha)</th>
<th>PO(_4)-P (gm/ha)</th>
<th>TOC (gm/ha)</th>
<th>TKN (gm/ha) (NF*)</th>
<th>TKN (gm/ha) (F*)</th>
<th>TP (gm/ha) (NF)</th>
<th>TP (gm/ha) (F)</th>
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<tr>
<td>2005</td>
<td>row crop</td>
<td>154</td>
<td>3633</td>
<td>269</td>
<td>1251</td>
<td>54909</td>
<td>1947</td>
<td>1594</td>
<td>750</td>
<td>304</td>
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<td></td>
<td>CRP</td>
<td>6</td>
<td>46</td>
<td>52</td>
<td>694</td>
<td>4732</td>
<td>436</td>
<td>689</td>
<td>319</td>
<td>248</td>
</tr>
<tr>
<td>2006</td>
<td>row crop</td>
<td>56</td>
<td>5213</td>
<td>740</td>
<td>713</td>
<td>45879</td>
<td>3514</td>
<td>4044</td>
<td>1513</td>
<td>870</td>
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<td>3105</td>
<td>805</td>
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<td>60165</td>
<td>2363</td>
<td>3773</td>
<td>1199</td>
<td>1200</td>
</tr>
<tr>
<td>2007</td>
<td>row crop</td>
<td>75</td>
<td>3204</td>
<td>659</td>
<td>2575</td>
<td>46649</td>
<td>7155</td>
<td>7370</td>
<td>2451</td>
<td>988</td>
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<tr>
<td></td>
<td>CRP</td>
<td>12</td>
<td>881</td>
<td>222</td>
<td>909</td>
<td>23699</td>
<td>1693</td>
<td>2556</td>
<td>656</td>
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<td>2008</td>
<td>row crop</td>
<td>63</td>
<td>5342</td>
<td>272</td>
<td>2791</td>
<td>52348</td>
<td>3492</td>
<td>2963</td>
<td>2011</td>
<td>1716</td>
</tr>
<tr>
<td></td>
<td>CRP</td>
<td>14</td>
<td>988</td>
<td>181</td>
<td>2000</td>
<td>55474</td>
<td>1591</td>
<td>1767</td>
<td>419</td>
<td>522</td>
</tr>
</tbody>
</table>

* Water samples filtered through 0.45 μm nitrocellulose membranes to produce the filterable (F) and nonfilterable (NF) nutrient components of TKN and TP.

**Figure 6.** Average monthly Secchi visibility or depth measurements (cm), suspended sediments (SS), and dissolved or filterable sediments (DS) from surface water samples taken from three sites on Beasley Lake from 1995 thru 2008.

Improvements in edge-of-field water quality were observed when evaluating differences in sediments and nutrients in runoff resulting from converting cropped land to CRP. All physical and chemical water quality data from the runoff from these drainage ditches provided support for the hypothesis that improvement in edge-of-field water quality can be demonstrated via land placed in the Conservation Reserve Program. Reductions of soil loss and reduction of nutrients were found from each storm event, each quarterly, annual, and total data. The impact of converting one third of the
cropped area into trees reduced the sediments leaving the watershed and entering the lake by an order of magnitude, resulting in improved water quality in Beasley Lake.

While lake nutrients had declined due to installation of structural conservation practices and implementation of conservation tillage within the watershed, conversion to CRP continued to contribute to decreasing concentrations of nutrients and improvement of water quality (Table 4). Comparing the mean concentrations of ammonium-nitrogen, nitrate-nitrogen, orthophosphate, and total phosphorus in lake water for the period following implementation of conservation tillage with the period following CRP conversion indicates a decrease in all four nutrients by 85%, 19%, 18% and 18%, respectively.

Table 3. Secchi visibility and sediment data from water samples from three sites on Beasley Lake.

<table>
<thead>
<tr>
<th>Year</th>
<th>Secchi Visibility (cm)</th>
<th>Total Sediments (mg/L)</th>
<th>Suspended Sediments (mg/L)</th>
<th>Filterable Sediments (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1995</td>
<td>18</td>
<td>232</td>
<td>179</td>
<td>52</td>
</tr>
<tr>
<td>1996</td>
<td>18</td>
<td>603</td>
<td>535</td>
<td>68</td>
</tr>
<tr>
<td>1997</td>
<td>16</td>
<td>270</td>
<td>203</td>
<td>67</td>
</tr>
<tr>
<td>1998</td>
<td>14</td>
<td>238</td>
<td>173</td>
<td>64</td>
</tr>
<tr>
<td><strong>Average from 1995-1998</strong></td>
<td><strong>16</strong></td>
<td><strong>333</strong></td>
<td><strong>273</strong></td>
<td><strong>63</strong></td>
</tr>
<tr>
<td>1999</td>
<td>8</td>
<td>286</td>
<td>227</td>
<td>64</td>
</tr>
<tr>
<td>2000</td>
<td>14</td>
<td>215</td>
<td>142</td>
<td>73</td>
</tr>
<tr>
<td>2001</td>
<td>26</td>
<td>149</td>
<td>90</td>
<td>59</td>
</tr>
<tr>
<td>2002</td>
<td>24</td>
<td>112</td>
<td>55</td>
<td>55</td>
</tr>
<tr>
<td>2003</td>
<td>35</td>
<td>95</td>
<td>45</td>
<td>50</td>
</tr>
<tr>
<td><strong>Average from 1999-2003</strong></td>
<td><strong>21</strong></td>
<td><strong>171</strong></td>
<td><strong>112</strong></td>
<td><strong>60</strong></td>
</tr>
<tr>
<td>2004</td>
<td>35</td>
<td>132</td>
<td>75</td>
<td>57</td>
</tr>
<tr>
<td>2005</td>
<td>40</td>
<td>126</td>
<td>72</td>
<td>54</td>
</tr>
<tr>
<td>2006</td>
<td>42</td>
<td>86</td>
<td>38</td>
<td>49</td>
</tr>
<tr>
<td>2007</td>
<td>45</td>
<td>97</td>
<td>47</td>
<td>50</td>
</tr>
<tr>
<td>2008</td>
<td>59</td>
<td>82</td>
<td>18</td>
<td>63</td>
</tr>
<tr>
<td><strong>Average from 2004-2008</strong></td>
<td><strong>44</strong></td>
<td><strong>105</strong></td>
<td><strong>50</strong></td>
<td><strong>54</strong></td>
</tr>
<tr>
<td><strong>Average from 1995-2008</strong></td>
<td><strong>26</strong></td>
<td><strong>180</strong></td>
<td><strong>120</strong></td>
<td><strong>60</strong></td>
</tr>
</tbody>
</table>

Table 4. Mean concentration of chemicals from all water samples of Beasley Lake from 2001 thru 2008 from before and after CRP.

<table>
<thead>
<tr>
<th>Years</th>
<th>Status of Watershed</th>
<th>NH$_4$-N (mg/L)</th>
<th>NO$_3$-N (mg/L)</th>
<th>ortho P (mg/L)</th>
<th>TP (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2001-2003</td>
<td>before CRP</td>
<td>0.058</td>
<td>0.141</td>
<td>0.698</td>
<td>0.227</td>
</tr>
<tr>
<td>2004-2008</td>
<td>after CRP</td>
<td>0.009</td>
<td>0.114</td>
<td>0.573</td>
<td>0.187</td>
</tr>
<tr>
<td>% diff</td>
<td>-85</td>
<td>-19</td>
<td>-18</td>
<td>-18</td>
<td>-18</td>
</tr>
</tbody>
</table>

Summary and Conclusions

This study of Beasley Lake Watershed was used to evaluate runoff from edge-of-field sites with various row crop management practices, and quantify effects of areas in the watershed that were shifted to forest (CRP). Approximately one-third of the Beasley Lake watershed (ca. 280 ha) was converted from cropped land to CRP beginning in 2003, and the remainder of the cropland is still managed for soybean, cotton, or corn production. Sub-drainage areas (1.2 to 6 ha) with similar topography and soil types were either cropped (three sites under reduced tillage crop production) or CRP (three CRP sites) and were instrumented in 2005 to collect water samples from field drainage slotted-inlet pipes during all surface runoff events. These runoff samples were analyzed for sediments, nutrients, and pesticides. Reducing soil loss and nutrient loads in runoff from edge-of-field through the use of BMPs results in lower sediments and agrichemicals entering Beasley Lake. Establishing trees
within CRP adjacent to oxbow lakes reduces the quantities of sediments and nutrients leaving the watershed as compared to reduced-till crop management techniques. The impact of converting one third of the cropped area into trees has reduced the sediments leaving the watershed by an order of magnitude resulting in improved water quality in Beasley Lake by July 2008.

Acknowledgements: The authors wish to thank Tim Sullivan, Calvin Vick, and John Massey for providing technical support and assistance.

References


Anaerobic Mesophilic and Thermophilic Treatment of Concentrated Latex Processing Wastewater in Two-Stage Upflow Anaerobic Sludge Blanket (UASB)

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Abstract: The objective of this study is to determine optimal conditions for operating the two-stage upflow anaerobic sludge blanket (UASB) used for treating wastewater from concentrated latex mills. Mesophilic and thermophilic conditions as well as hydraulic retention time (HRT), and pH were determined. Effect of NH3 on treatment inhibition was also investigated. The results indicated that mesophilic condition (35 °C) was an optimal temperature, whereas the pH of system should be controlled at 7 to prevent rubber coagulation. The HRT at 24 hrs and 48 hrs were optimal HRT for acid tank and UASB tank, respectively. In case of NH3, inhibition on methane producing bacteria was observed at 1,000 mg/l NH3-N, and strong inhibition occurred at 3,000 mg/l NH3-N, since % COD removal was relatively reduced from 37.32 mg/l (at 1,000 mg/l NH3-N) to 7.98 mg/l. The two-stage UASB was then applied with above-mentioned optimal conditions with real wastewater at latex mill. It was found that methane production was about 0.116 l CH4/g COD removed (16.257-22.76 m3CH4/d), and average COD and SS removal efficiency were about 81.08 % and 94.22 %, respectively. In case of SS removal, the results reveal that the two-stage UASB is capable to overcome limitation of the single-stage UASB in treating concentrated latex effluent.

Keywords: Two-stage UASB, Concentrated latex, Mesophilic, Thermophilic, Ammonia

Introduction

Thailand is an important rubber producing country. About 35% of the latex produced worldwide is from Thailand (OAE, 2007). Since 2003, Thailand has become the world’s largest natural rubber (NR) producer. In 2008, the fresh latex production in Thailand was about 3 million ton with an average yield of 5.64 ton fresh latex per hectare (OAE, 2007). Concentrated latex is one important product with an annual production capacity of about 2.92x106 tons, and has prosperous incremental trend (RRIT, 2000). However, its production process has resulted in several environmental problems including air pollution, water pollution and solid waste production. Since natural rubber products are being exported to the international market, it has been challenging for Thai rubber entrepreneurs to seek for appropriate environmental measures to produce environmentally friendly rubber products. Among these problems, water pollution has been paid much attention in Thailand.

Concentrated latex processing wastewater mainly contains BOD, COD, NH3-N, organic-N and phosphate. Intanmanee (1997) reported that effluent COD from latex mill in Thailand was in the range of 25,000 – 35,000 mg/l, whereas concentration of nitrogen in terms of TKN, NH3, NH2 and NO3 were about 550-1,300 mg/l, 200 mg/l, 40 mg/l and 10 mg/l, respectively. Rakkerd (1998) reported that concentration of P (phosphorus) was about 40 mg/l. A schematic diagram of concentrated latex production indicating sources of wastewater is illustrated in Figure.1. Washing and centrifugation are the main sources of wastewater containing large amount of ammonia and phosphorus (from DAP-diammonium phosphate), whereas wastewater from skim latex production is highly acid due to the use of sulphuric acid for coagulation. Current wastewater treatment systems in Thailand for concentrated latex mills are combination of anaerobic pond and aerobic pond, such as aerated lagoon (AL) and
oxidation pond (OP). However, it is regularly found that the treated effluent from these processes does not meet Thailand industrial effluent standards (Intarasangka, 2003).

To overcome the mentioned limitations of aerobic treatment, several anaerobic wastewater treatment processes have been applied. Ngyeun (1999) investigated the performance of the lab-scale single stage UASB treating rubber processing wastewater in Vietnam, and found that COD removal efficiency was about 80-88% at organic loading rate of 28.5 kg COD/ m$^3$.day. However, he found that the SS originating from rubber particles adversely affects the single stage UASB. Moreover, the performance of the single stage system is limited for the wastewater containing slowly degradable solid and toxic substances like latex processing wastewater. Application of the two-stage system, which separates a reactor for different group of bacteria (acid former and methane former), can reduce those limitations. However, no study on the two-stage UASB of concentrated latex processing wastewater has been yet reported.

![Figure 1. Schematic diagram of concentrated latex production.](image-url)
The objective of this study is to determine treatment performance of the two-stage UASB treating wastewater produced from concentrated latex production in mesophilic and thermophilic condition. Treatment performance was evaluated by determination of COD and SS removal efficiencies, methane production and VFA accumulation. Assessment of the specific methanogenic activity (SMA) of different sludge to be used as seed is also reported. Effect of ammonia (NH₃-N), which is mainly used in concentrated latex production, on treatment inhibition is also investigated.

Materials and methods

Experimental lab-scale reactors

A two-stage UASB consisted of one acid tank and one UASB reactor had been set up. The acid tank, which made of PVC, was 26.5 cm. in diameter and 60 cm. in height and had a working volume of 24.8 liter. The UASB reactor consisted of outer and inner columns both were made of acrylic. The inner column was 6 cm. in diameter and 120 cm. in height and had working volume of 3.523 liter (excluding volume of a gas-solid separator installed at the upper zone of the column). Water sampling ports were installed at three different levels of the column. The outer column, which was 12 cm. in diameter, worked as a water jacket through installation of a heater to control temperature of the UASB reactor. A schematic of the experimental set up of the two-stage UASB reactor is illustrated in Figure 2.

Seed

Different sludge was taken from three sources including fish cannery, frozen food industry and latex mills, which are major industries in the south of Thailand, to evaluate the specific methanogenic activity (SMA). The SMA assessment is based on Tay and Yan (1996). The sludge is determined using a 250 l Kimax flask, and the substrate is D-glucose. An initial substrate (0.5-1.5 g) to sludge (0.5-1.5 g VSS) ratio of 0.5-1.5 is maintained. After flushing the medium with nitrogen gas, the flask was sealed and incubated at 30 °C in a water bath shaker. The biogas produced is passed through a 2 mol/l of NaOH solution saturated with NaOH to absorb CO₂ and the remaining CH₄ was collected and measured hourly over a 10-hr period.

Nutrients

A nutrient and trace elements solution was prepared followed Hulshoff Pol (2004). It was supplied to the influent wastewater by preparing stock solution and use of 6 ml nutrient solution and 0.1 ml trace-solution for 1 l influent. The composition of these stock solutions is shown in Table 1.
Determination of HRT in the acid forming phase

Six acid tanks with a working volume of 24.8 liters for six different HRT (12, 18, 24, 36, 48 and 72 hrs) were set up. Each acid tank was inoculated with seed (20% v/v) and wastewater from latex mill. The COD concentration was controlled at about 4,000 mg/l. VFA accumulation and sCOD were evaluated.

Table 1. Composition of nutrient solution and trace element supplied to the influent.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>mg/l</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Nutrient solution</strong></td>
<td></td>
</tr>
<tr>
<td>NH₄Cl</td>
<td>1044</td>
</tr>
<tr>
<td>K₂HPO₄</td>
<td>169.8</td>
</tr>
<tr>
<td>(NH₄)₂SO₄</td>
<td>169.8</td>
</tr>
<tr>
<td>MgCl₂·6 H₂O</td>
<td>150</td>
</tr>
<tr>
<td>KCl</td>
<td>270</td>
</tr>
<tr>
<td>Yeast extract</td>
<td>19.8</td>
</tr>
<tr>
<td><strong>Trace Element</strong></td>
<td></td>
</tr>
<tr>
<td>FeCl₂·4H₂O</td>
<td>0.2</td>
</tr>
<tr>
<td>H₃BO₃</td>
<td>0.005</td>
</tr>
<tr>
<td>ZnCl₂</td>
<td>0.005</td>
</tr>
<tr>
<td>CuCl₂·2H₂O</td>
<td>0.0038</td>
</tr>
<tr>
<td>MnCl₂·4H₂O</td>
<td>0.05</td>
</tr>
<tr>
<td>(NH₄)₆Mo₇O₂⁴·4H₂O</td>
<td>0.005</td>
</tr>
<tr>
<td>AlCl₃·6H₂O</td>
<td>0.009</td>
</tr>
<tr>
<td>CoCl₂·6H₂O</td>
<td>0.2</td>
</tr>
<tr>
<td>NiCl₂·6H₂O</td>
<td>0.0092</td>
</tr>
<tr>
<td>Na₂SeO₃·5H₂O</td>
<td>0.0164</td>
</tr>
<tr>
<td>EDTA C₁₀H₁₀N₂O₈</td>
<td>0.1</td>
</tr>
<tr>
<td>Resazurine</td>
<td>0.02</td>
</tr>
<tr>
<td>36% HCl</td>
<td>0.0001 (ml)</td>
</tr>
</tbody>
</table>

Effect of ammonia: Batch experiment

Serum bottle with a working volume of 1,000 ml was used as a reactor (Figure 3). The bottle was sealed with aluminum screw caps and butyl rubber septum. The concentrated latex processing wastewater plus additional nutrient solution and trace elements (Table 1) was fed to the bottle. The influent COD concentration and pH were controlled at about 1,200 mg/l, and 7, respectively. To investigate effect of ammonia, the influent NH₃-N concentrations varied at 100, 500, 1,000 and 3,000 mg/l. Temperature of the reactor was controlled at 35 °C. Methane production was measured by substitution of 5% NaOH.

Figure 3 Serum bottle used as a reactor in batch experiment. Source: Nguyen (1999)
**UASB start up and operating conditions**

The UASB reactor was inoculated with seed (selected from 2.1) (20% v/v) and 10% of concentrated wastewater plus 90% from D-glucose. The concentration of wastewater was then gradually increased in a stepwise manner to 20%, 50%, 80% and finally at 100% (COD concentration of 4,000 mg/l). The pH was adjusted to about 7 by adding NaHCO₃. The reactor was then operated until it reached steady state. After the start-up period, efficiencies of COD and SS removal, methane production and VFA accumulation were determined at different HRT (12, 24, 48 and 72 hrs.) at mesophilic temperature (35 °C) and thermophilic temperature (55 °C).

**Analytical procedures**

Influent COD and effluent COD were determined by the closed reflux titrimetric, whereas suspended solid (SS) was determined by gravimetric method (APHA et al., 1998). Methane production was measured by a liquid displacement method. VFA was measured by direct titration method following Moosbrugger et al. (1990). A pH was measured using Thermo Orion’s pH meter (model 420A⁻).

**Results and Discussion**

**Characteristic of concentrated latex processing wastewater**

Characteristic of concentrated latex processing wastewater in Thailand largely depends on latex production capacity, which is directly associated with season. The production capacity is high during May-September, and declines during October-January and February-April. Characteristic of concentrated latex processing wastewater throughout a year is presented in Table 2.

From Table 2 it is found that current COD, BOD and SS values of concentrated latex processing wastewater in Thailand, on average, are lower than those of in the past (In year 2000, COD, BOD and SS were about 9,000 mg/l, 6,500 mg/l and 550 mg/l, respectively (Phoolphundh and Wongkittiwimon, 2000)). One possible explanation is that rubber price in Thailand is currently high, and the manufacturers have the incentive to extract as much rubber content from wastewater as possible. This is achieved for instance, by making skim rubber from skim latex by coagulation of sulfuric acid and making rubber gel by addition of polymer. As a result, the wastewater contains less rubber content. Effluent COD and BOD are consequently lower.

**Table 2** Characteristic of concentrated latex processing wastewater in Thailand.

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Range</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>3.9-4.4</td>
<td></td>
</tr>
<tr>
<td>Suspended solid</td>
<td>265-856</td>
<td>mg/l</td>
</tr>
<tr>
<td>Volatile solid</td>
<td>154-292</td>
<td>mg/l</td>
</tr>
<tr>
<td>Soluble solid</td>
<td>7,780-8,650</td>
<td>mg/l</td>
</tr>
<tr>
<td>COD</td>
<td>3,890-4,860</td>
<td>mg/l</td>
</tr>
<tr>
<td>BOD</td>
<td>2,400-2,860</td>
<td>mg/l</td>
</tr>
<tr>
<td>Sulfate</td>
<td>1,247-1,440</td>
<td>mg/l</td>
</tr>
<tr>
<td>TKN</td>
<td>836-1397</td>
<td>mg/l</td>
</tr>
<tr>
<td>Ammonia-N</td>
<td>316-578</td>
<td>mg/l</td>
</tr>
<tr>
<td>Total-P</td>
<td>86.46-126</td>
<td>mg/l</td>
</tr>
<tr>
<td>Calcium</td>
<td>10.69-16.30</td>
<td>mg/l</td>
</tr>
<tr>
<td>Cobalt</td>
<td>nd</td>
<td>mg/l</td>
</tr>
<tr>
<td>Nickel</td>
<td>nd</td>
<td>mg/l</td>
</tr>
<tr>
<td>Zinc</td>
<td>nd-0.274</td>
<td>mg/l</td>
</tr>
<tr>
<td>Copper</td>
<td>nd-0.022</td>
<td>mg/l</td>
</tr>
<tr>
<td>Iron</td>
<td>0.843-4.184</td>
<td>mg/l</td>
</tr>
<tr>
<td>Magnesium</td>
<td>0.168-0.173</td>
<td>mg/l</td>
</tr>
<tr>
<td>Chloride</td>
<td>7.4-17.1</td>
<td>mg/l</td>
</tr>
</tbody>
</table>

*nd = not detected*
Selection of sludge for UASB seed

Specific methanogenic activity (SMA) of sludge

In this study, sludge from other treatment plant will be used as seed in the UASB process. Sludge from fish cannery, frozen food industry and latex mills were determined for the specific methanogenic activity (SMA). Results in Table 3 indicated that sludge from fish cannery resulted in the highest SMA followed by sludge from frozen food and latex mill. This means that if sludge from latex mill is used as seed in the UASB, it would need longer time in the UASB start-up than those of other two sources. However, sludge from latex mill was chosen to be used as seed in the UASB operation, because sludge from latex mill is accustomed with the wastewater, and is tolerant to toxic compounds contained in the wastewater. Another reason is that if sludge from latex mill, which resulted in the lowest SMA, is capable to work in the UASB, then the use of other sludge as seed is also possible.

Table 3. Analysis of Specific Methanogenic Activity (SMA) of sludge from fish cannery, frozen food industry, and latex mill.

<table>
<thead>
<tr>
<th>Source of sludge</th>
<th>SMA g COD/g VSS</th>
<th>SD kg/m³</th>
<th>TSS %</th>
<th>SVI ml/g SS</th>
<th>VSS %</th>
<th>Ash %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fish cannery</td>
<td>0.13-0.18</td>
<td>1020</td>
<td>18.79</td>
<td>45.6-49.8</td>
<td>78.22</td>
<td>2.99</td>
</tr>
<tr>
<td>Frozen food</td>
<td>0.11-0.13</td>
<td>1135</td>
<td>12.56</td>
<td>42.6-44.2</td>
<td>85.26</td>
<td>2.18</td>
</tr>
<tr>
<td>Latex mill</td>
<td>0.08-0.11</td>
<td>978</td>
<td>7.69</td>
<td>41.2-43</td>
<td>89.98</td>
<td>2.33</td>
</tr>
</tbody>
</table>

a SD = Specific Density; b TSS = Total Suspended Solid; c SVI = Sludge Volume Index; d VSS = Volatile Suspended Solid

Effect of temperature and pH on anaerobic biodegradation in latex-mill wastewater with granular sludge

The influence of temperature on anaerobic biodegradation was determined at 35 °C (Mesophilic) and 55 °C (Thermophilic). It was found that the average SMA at 35 °C and 55 °C are 0.096 g COD/ g VSS and 0.073 g COD/ g VSS, respectively. These results indicated that both SMA and COD removal efficiency are higher at 35 °C (Figure 4). This is because at higher temperature viscosity of wastewater is increased due to reaction of sulphur in rubber particle (Chaovanich and Nithi-Uthai, 2005). Higher wastewater viscosity limits movement of the granular sludge, and this consequently reduces treatment efficiency. Another reason is that typical temperature of wastewater from concentrated latex mill in Thailand is about 30 – 35 °C (mesophilic condition), and seed from latex mill is accustomed to such temperature range. If the system is operated at thermophilic condition (55 °C), the start up period would take longer time than that of mesophilic condition (35 °C).

Analysis about effect of pH on anaerobic biodegradation revealed that the highest SMA (0.080 g COD/ g VSS) was found at pH 7 (Table 4). To achieve high treatment performance, maintaining pH at 7 is therefore necessary. It was found that if pH is lower than 7, the treatment performance would be dropped because of rubber coagulation. The coagulated rubber particles would combine with the granular sludge, and, as a result, reduce the treatment efficiency.

Effect of NH₃-N on treatment performance inhibition

The influent NH₃-N concentrations were varied at 100, 500, 1000 and 3000 mg/l to investigate the inhibition on anaerobic activities. From Table 5, it was clear that COD removal efficiency decreased, as NH₃-N concentration was increased. It can also be observed that NH₃-N concentration at 1,000 -3,000 mg/l resulted in toxicity on MPB, since methane production was not produced in such concentrations. This is in line with study of McCarty (1964) who reported that NH₃-N concentration at 1,500 -3,000 mg/l resulted in inhibition of anaerobic bacteria, especially at high pH. He also reported that the NH₃-N would be toxic to anaerobic bacteria, if the concentration was exceeded 3,000 mg/l. However, NH₃-N concentration in CLPW was in range of 300-500 mg/l, and it was found that methane was still produced (0.158 l/g COD) at 500 mg/l NH₃-N concentration. Therefore, it can be concluded that NH₃-N concentration in CLPW was not significantly toxic to MPB in anaerobic treatment.
Figure 4 Centrifuged COD in SMA analysis at 35 ºC and 55 ºC.

Table 4 Effect of pH on anaerobic biodegradation in latex-mill wastewater with granular sludge.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average SMA (gCOD/gVSS)</td>
<td>0.038</td>
<td>0.075</td>
<td>0.080</td>
<td>0.078</td>
</tr>
<tr>
<td>Residual COD (mg/l) (Centrifuged COD)</td>
<td>1,520</td>
<td>800</td>
<td>160</td>
<td>560</td>
</tr>
<tr>
<td>% COD removal</td>
<td>34.48</td>
<td>65.52</td>
<td>93.10</td>
<td>75.86</td>
</tr>
<tr>
<td>Volatile Fatty Acid (VFA) (mg/l)</td>
<td>686</td>
<td>778</td>
<td>1,020</td>
<td>998</td>
</tr>
<tr>
<td>Suspended Solid (SS) (mg/l)</td>
<td>26,560</td>
<td>30,560</td>
<td>33,460</td>
<td>31,940</td>
</tr>
<tr>
<td>Volatile Suspended Solid (VSS) (mg/l)</td>
<td>20,980</td>
<td>20,380</td>
<td>26,920</td>
<td>22,640</td>
</tr>
<tr>
<td>Fixed solid (mg/l)</td>
<td>5,580</td>
<td>10,180</td>
<td>6,540</td>
<td>9,300</td>
</tr>
</tbody>
</table>

The pH also plays important role on effect of NH$_3$-N. If pH is higher than 7.2, ammonium ion (NH$_4^+$) would convert to toxic ammonia (NH$_3$) (equation 1). However, if pH is lower than 7.2 (NH$_3$-N concentration at 100 and 500 mg/l), less toxic (non-toxic) NH$_4^+$ form would dominate

$$\text{NH}_4^+ + \text{H}^+ \rightarrow \text{NH}_3 + \text{H}_2\text{O}$$

Table 5 Treatment performance of the two-stage UASB at NH$_3$-N 100, 500, 1000 and 3000 mg/l

<table>
<thead>
<tr>
<th>NH$_3$-N (mg/l)</th>
<th>COD removal (%)</th>
<th>NH$_3$-N removal (%)</th>
<th>TKN (mg/l)</th>
<th>MLSS (mg/l)</th>
<th>pH</th>
<th>Vol. gas (l CH$_4$/g COD removed)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>70.17</td>
<td>55.9</td>
<td>61.25</td>
<td>3601.18</td>
<td>6.46</td>
<td>0.273</td>
</tr>
<tr>
<td>500</td>
<td>57.82</td>
<td>48.434</td>
<td>319.6</td>
<td>3422.73</td>
<td>6.86</td>
<td>0.158</td>
</tr>
<tr>
<td>1000</td>
<td>37.32</td>
<td>40.386</td>
<td>667.39</td>
<td>3518.36</td>
<td>7.15</td>
<td>-</td>
</tr>
<tr>
<td>3000</td>
<td>7.98</td>
<td>71.35</td>
<td>1667.26</td>
<td>3392.55</td>
<td>7.63</td>
<td>-</td>
</tr>
</tbody>
</table>

Accumulation of toxic NH$_3$-N damaged granular sludge. This can be observed from reduction of MLSS from initial 3,896 mg/l to 3,518 mg/l, as NH$_3$-N concentration was increased to 1,000 mg/l. Damaged granular sludge resulted in increase of organic N, which consequently increased TKN concentration. Figure 5 compared normal granular sludge and damaged granular sludge at high NH$_3$-N concentration (3,000 mg/l).
Figure 5. Comparison of (5.1) normal granular sludge, and (5.2) damaged granular sludge at 3,000 mg/l NH3-N (captured by Olympus’ stereoscope Model DP 12 SZ-CTV).

Start up of the two-stage UASB

Optimal HRT of the acid forming phase

From Table 6 which presents the results of different HRT in the acid forming phase, it was found that HRT at 24 hrs is the optimal HRT, because it resulted in the highest VFA production (1,421.19 mg CH3COOH/l). The efficiency of COD and SS removal at this HRT is 50.71% and 68.53%, respectively. Nevertheless, it is worth noting that lower pH resulting from increase of VFA accumulation causes coagulation of rubber particle. This is because stability of rubber particle, which is wrapped by protein and has negative charge at its surface, is weakened when the pH is lowered (more H+ in the system). Consequently, coagulated rubber may cause clogging in the subsequent UASB phase. To avoid this problem, pH of the effluent from acid tank should be controlled at 6.5-7.5.

Table 6 Analysis of different HRT in the acid forming phase.

<table>
<thead>
<tr>
<th>HRT  (hr)</th>
<th>Organic loading (kgCOD/m³ d)</th>
<th>COD removal (%)</th>
<th>SS removal (%)</th>
<th>pH</th>
<th>ORP  (mV)</th>
<th>VFA (mgCH3COOH/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>12</td>
<td>7.961</td>
<td>40.37</td>
<td>54.67</td>
<td>6.98</td>
<td>-318.05</td>
<td>511.46</td>
</tr>
<tr>
<td>18</td>
<td>5.306</td>
<td>44.16</td>
<td>64.11</td>
<td>6.79</td>
<td>-309.33</td>
<td>792.65</td>
</tr>
<tr>
<td>24</td>
<td>3.980</td>
<td>50.71</td>
<td>68.53</td>
<td>6.85</td>
<td>-265.77</td>
<td>1421.19</td>
</tr>
<tr>
<td>36</td>
<td>2.653</td>
<td>52.86</td>
<td>66.79</td>
<td>6.83</td>
<td>-326.91</td>
<td>974.15</td>
</tr>
<tr>
<td>48</td>
<td>1.990</td>
<td>52.89</td>
<td>71.16</td>
<td>6.80</td>
<td>-326.52</td>
<td>828.69</td>
</tr>
<tr>
<td>72</td>
<td>1.325</td>
<td>56.58</td>
<td>77.22</td>
<td>6.66</td>
<td>-312.14</td>
<td>826.31</td>
</tr>
</tbody>
</table>

UASB start up

The UASB reactor was inoculated with seed (20% v/v) taken from concentrated latex mill and 10% (COD concentration of 400 mg/l) of concentrated latex processing wastewater plus 90% from D-glucose and supplementary substrates as mentioned in section 2.4. The concentration of wastewater was then gradually increased in a stepwise manner to 20%, 50%, 80% and finally 100% (COD concentration of 4,000 mg/l). Upflow velocity was controlled at 0.25 – 2 m/hr to prevent sludge wash out. NaHCO3 was used to maintain pH of inflow wastewater at 7.

It can be observed that 67 days after start up newly formed granular appeared in the reactor, and the granular was completely formed at day 89 (Table 7). Diameter of granular is about 1-2 mm. (Figure 5.1). Rubber particle contained in concentrated latex processing wastewater is polymer, and therefore is an important factor to enhance granular formation by bridging flocculation of bacterial particles. Table 7 also shows that the formed granular resulted in high settling time, which consequently allows higher upflow velocity. Higher settling time also reduces sludge wash out.
Table 7 Results from the UASB start up.

<table>
<thead>
<tr>
<th>Day</th>
<th>MLSS (mg/l)</th>
<th>MLVSS (mg/l)</th>
<th>SVI (ml/g)</th>
<th>SV 30 (ml/l)</th>
<th>Settling time (m/hr)</th>
<th>Granular size (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>14</td>
<td>26,520</td>
<td>17,460</td>
<td>6.34</td>
<td>168</td>
<td>6.7</td>
<td>-</td>
</tr>
<tr>
<td>22</td>
<td>18,180</td>
<td>14,120</td>
<td>10.01</td>
<td>182</td>
<td>8.9</td>
<td>-</td>
</tr>
<tr>
<td>32</td>
<td>21,700</td>
<td>26,580</td>
<td>8.52</td>
<td>185</td>
<td>12.6</td>
<td>-</td>
</tr>
<tr>
<td>48</td>
<td>30,266</td>
<td>22,860</td>
<td>6.34</td>
<td>192</td>
<td>21.27</td>
<td>-</td>
</tr>
<tr>
<td>65</td>
<td>22,033</td>
<td>19,966</td>
<td>9.12</td>
<td>201</td>
<td>32.14</td>
<td>-</td>
</tr>
<tr>
<td>72</td>
<td>38,500</td>
<td>29,993</td>
<td>5.532</td>
<td>213</td>
<td>35.89</td>
<td>1</td>
</tr>
<tr>
<td>76</td>
<td>33,600</td>
<td>23,266</td>
<td>6.64</td>
<td>223</td>
<td>45.6</td>
<td>1</td>
</tr>
<tr>
<td>82</td>
<td>30,366</td>
<td>21,380</td>
<td>8.20</td>
<td>249</td>
<td>56.89</td>
<td>2</td>
</tr>
<tr>
<td>90</td>
<td>33,200</td>
<td>21,520</td>
<td>7.71</td>
<td>256</td>
<td>63.1</td>
<td>1-2</td>
</tr>
<tr>
<td>Mean</td>
<td>28,262.78</td>
<td>21,905.00</td>
<td>7.60</td>
<td>207.67</td>
<td>31.45</td>
<td>1-2</td>
</tr>
</tbody>
</table>

Optimal HRT of the UASB phase

Table 8 presents the results of COD and SS removal efficiencies, methane production, and VFA accumulation at different HRT (12, 24, 48 and 72 hrs). It was found that HRT at 48 hrs resulted in the highest biogas production (0.116 l CH₄/g COD removed), 73.66% of COD removal efficiency and 78.88% of SS removal efficiency. Although the highest COD and SS removal (81.94% and 90.42%, respectively) were found at HRT 72 hrs, the HRT at 48 hrs was considered an optimal HRT for operation in the UASB phase. This is because the HRT at 72 hrs resulted in high alkalinity (3,172.88 mg CH₃COOH/l) and pH (7.83). Such conditions resulted in reduction of granular movement, which consequently reduced treatment efficiency.

Table 8 Analysis of different HRT in the UASB reactor.

<table>
<thead>
<tr>
<th>HRT (hr)</th>
<th>Organic loading (kgCOD/m³ d)</th>
<th>COD removal (%)</th>
<th>SS removal (%)</th>
<th>Vol. gas (l/d)</th>
<th>VFA mg/l as CH₃COOH</th>
<th>Alkalinity mg/l as CaCO₃</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>12</td>
<td>8.454</td>
<td>40.14</td>
<td>52.07</td>
<td>0.505</td>
<td>980</td>
<td>1808.53</td>
<td>7.07</td>
</tr>
<tr>
<td>24</td>
<td>4.228</td>
<td>65.38</td>
<td>61.12</td>
<td>0.593</td>
<td>1050</td>
<td>2025.41</td>
<td>7.26</td>
</tr>
<tr>
<td>48</td>
<td>2.114</td>
<td>73.66</td>
<td>78.88</td>
<td>0.745</td>
<td>1350</td>
<td>2850.15</td>
<td>7.35</td>
</tr>
<tr>
<td>72</td>
<td>1.409</td>
<td>81.94</td>
<td>90.42</td>
<td>0.661</td>
<td>1140</td>
<td>3172.88</td>
<td>7.83</td>
</tr>
</tbody>
</table>

Effect of pH and temperature on treatment performance

Effect of pH

Figure 6 illustrates change of pH throughout continuous run period (at HRT = 48 hrs). At initial stage, it can be observed that pH was sharply increased due to increasing alkalinity caused by effluent recirculation. The pH was then steady when the system reached equilibrium. This reveals that the effluent recirculation is very important process for operating the system, because it prevents the rubber particle coagulation which occurs at acidic condition (pH < 6). Besides increasing alkalinity in the system, the effluent recirculation also dilutes the concentration of some inhibitors (e.g. ammonia and sulfate), and consequently reduce the adverse effect of these inhibitors.

It should be noted that if Ca²⁺ is present in the wastewater, it can be combined with CO₃²⁻ and form CaCO₃ which can reduce acetic acid in the system as described in the following equation.

\[
2\text{CaCO}_3 + 2\text{CH}_3\text{COOH} \rightarrow \text{Ca(HCO}_3\text{)}_2 + \text{Ca(CH}_3\text{COO)}_2
\]

As a result, reduction of acetic acid lowers gas generation rate. This is in line with study of McCarty and Mckinney (1961) who reported that concentration of Ca²⁺ at 2,500-4,000 mg/l inhibits system performance, and strongly inhibits at 8,000 mg/l. Nevertheless results from analysis of trace element (Table 9) indicated that Ca²⁺ concentration in latex processing wastewater is quite low (10-20 mg/l) and it can be concluded that such concentration does not inhibit treatment performance.
In contrast, Lettinga et al. (1980) reported that Ca(OH)$_2$ used by farmer to preserve field latex enhances sludge settleability and increases solid retention time in the reactor. Such conditions allow higher organic loading rate applied to the system.

**Table 9** Analysis of Ca$^{2+}$ and other trace elements in latex processing wastewater.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Result (mg/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca</td>
<td>10.69-20.64</td>
</tr>
<tr>
<td>Zn</td>
<td>nd-4.058</td>
</tr>
<tr>
<td>Cu</td>
<td>nd-0.718</td>
</tr>
<tr>
<td>Fe</td>
<td>0.948-4.716</td>
</tr>
<tr>
<td>Mg</td>
<td>0.168-36.65</td>
</tr>
</tbody>
</table>

**Comparison of treatment performance of the two-stage UASB at mesophilic and thermophilic conditions**

At HRT 24 hrs in acid tank and HRT 48 hrs in UASB reactor, the two-stage UASB was operated at 35°C and 55°C. The results presented in Table 10 show that operation at 35°C resulted in higher COD removal efficiency than that of at 55°C. During the experiment it can be observed that more rubber particle was accumulated at 55°C. This can be described that viscosity of remaining rubber particle, which is polymer substance, is increased when temperature is raised. The rubber particle then obstructs flow of wastewater and the granular sludge. As a result, the efficiency of COD was decreased.

**Table 10** Treatment performance of the two-stage UASB at 35°C and 55°C.

<table>
<thead>
<tr>
<th>Temp $^\circ$C</th>
<th>COD removal (%)</th>
<th>SS removal (%)</th>
<th>ORP (mV)</th>
<th>Alkalinity mg CH$_3$COOH/l</th>
<th>pH</th>
<th>Vol. gas (l/d)</th>
</tr>
</thead>
<tbody>
<tr>
<td>35</td>
<td>82.47</td>
<td>82.41</td>
<td>-444.37</td>
<td>1162.46</td>
<td>7.00</td>
<td>0.505</td>
</tr>
<tr>
<td>55</td>
<td>80.08</td>
<td>84.14</td>
<td>-437.29</td>
<td>1515.38</td>
<td>7.06</td>
<td>0.593</td>
</tr>
</tbody>
</table>

**Application of the two-stage UASB with real wastewater at latex mill**

The two-stage UASB was applied at latex mill with optimum HRT (24 hrs in acid forming tank, and 48 hrs in UASB tank), optimum pH (7) and optimum temperature (35°C), which were determined in above-mentioned analyses. Results of COD removal, SS removal, NH$_3$-N and methane production are shown in Figure 7, 8, 9 and 10, respectively.
COD values of influent were about 4,000 mg/l, whereas SS values fluctuate between 250-500 mg/l because of variation of field latex quality. At the initial stage efficiencies of COD and SS removal were not high, because it was the stage that bacteria assimilated to the wastewater. COD and SS removal efficiencies were then higher until the system reached the steady state (Figure 7, 8). According to Thailand industrial effluent standard, average effluent SS 21.5 mg/l was lower than that of mentioned in the standard (50 mg/l), but average effluent COD 573.3 mg/l did not meet the standard (120 mg/l). Other subsequent treatments should therefore be combined.

Figure 7. Influent COD and effluent COD after treating by the two-stage UASB.

Figure 8. Influent SS and effluent SS after treating by the two-stage UASB.

Figure 9 presents production of total gas and methane. Methane was found at 60-70% of total gas. According to Hawkes (1979) who reported that biogas containing 59% of methane releases energy by about 22 MJ/m³, methane production from application of the two-stage UASB to latex mill is estimated by about 0.116 l CH₄/g COD removed (16.257-22.76 m³CH₄/d), which is equivalent to 357.654-500.74 MJ/d. Figure 10 showed that NH₃-N influent was in the range of 280 -500 mg/l. The NH₃-N influent was in the form of free NH₃ which its level did not inhibit microbial activity. Nevertheless, the pH was controlled at about 7 during operating at latex mill, the NH₃-N was therefore in the form of NH₄⁺ which is low toxicity. Therefore, when the system reached the steady state, the NH₃-N effluent was lower than 100 mg/l. Such concentration has no toxicity to aquatic organism.
Conclusion

This study aims to investigate treatment performance of the two-stage UASB applied to concentrated latex processing wastewater in Thailand. The first step was to determine the optimal conditions including HRT in acid tank and UASB tank, pH, and temperature (mesophilic and thermophilic). It was found that HRT at 24 hrs and 48 hrs were optimal HRT for acid tank and UASB tank, respectively. The pH of system should be controlled at 7 to achieve high treatment performance. This is because if pH is lower than 7, rubber particles would be coagulated, and then combine with the granular sludge. As a result, the treatment efficiency would be reduced. In case of temperature, mesophilic condition (35 °C) was found to be an optimal temperature because it resulted in higher COD removal efficiency than that of thermophilic condition (55 °C). This is because at higher temperature viscosity of wastewater is increased due to reaction of sulphur in rubber particle. Higher wastewater viscosity limits movement of the granular sludge, and this consequently reduces treatment efficiency.

Second, effect of ammonia nitrogen (NH₃-N) on treatment performance inhibition was investigated. In batch experiment, it was found that inhibition on anaerobic bacteria was initially observed at 1,000 mg/l NH₃-N. Strong inhibition occurred at 3,000 mg/l NH₃-N, since % COD removal was relatively reduced from 37.32 mg/l (at 1,000 mg/l NH₃-N) to 7.98 mg/l. NH₃-N concentration at 100 and 500 mg/l, which were in the range of NH₃ presented in the real concentrated latex processing wastewater, did not result in inhibition on methane producing bacteria, since methane generation was still detected. In continuous experiment which the influent NH₃-N was controlled at
1,000 mg/l, it was found that the steady state was reached at day about 60. The maximum treatment efficiency was then reached at day about 100, which %COD removal, % NH₃-N removal and % TKN removal were 65.3, 68.7 and 73.2, respectively.

Finally, the two-stage UASB was then applied with above-mentioned optimal conditions with real wastewater at latex mill. It was found that methane production was about 0.116 l CH₄/g COD removed (16.257-22.76 m³CH₄/d), and average COD and SS removal efficiency were 81.08 % and 94.22 %, respectively. In case of SS removal efficiency, the result reveals that the two-stage UASB is capable to overcome the limitation of SS removal of the single-stage UASB treating concentrated latex effluent (Nguyen, 1999). This is because in the two-stage UASB the HRT is longer than that of in the single-stage UASB. Rubber particle containing in concentrated latex wastewater is complex polymer which is slowly degradable substance, and cannot be completely hydrolyzed in the single-stage UASB. Different conditions controlled for different group of bacteria (acid and methane former) in separate reactors in the two-stage UASB also enhance the SS treatment efficiency.

References


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Electroclarification: A Means for Decolourization of Sugar Cane Juice using Aluminium Alloy Al1050/ Polyaniline Modified Electrode

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Abstract: For electroclarification of sugar cane juice to produce high quality sugar thereby avoiding the use of hazardous chemicals, aluminum alloy Al1050 electrodes modified with a protective layer of polyaniline coating are used. Corrosion studies on these modified electrodes were investigated by using anodic potentiodynamic and Tafel polarization techniques. The results show a remarkable corrosion potential shift towards noble values, consistent with the formation of a compact polyaniline/phosphate film on the electrode surface. The polyaniline/phosphate coated aluminium Al1050 electrodes are then used for studying the electroclarification of sugar cane juice to decolorize its colorants. Successful electroclarification process is achieved by electrolysis of the aqueous cane juice solution at pH 7.0 (0.05 M phosphate) at a potential of -0.51 V for a period of 20 min. These simple procedures provide an energy efficient and environmentally friendly protocol that could be industrially utilized to replace the conventional clarification processes in sugar productions.

Key Words: Corrosion Studies, Aluminium alloy Al1050, Polyaniline/phosphate, Sugar Cane, Electro-clarification.

Introduction

In the technology of sugar production, separation of non-sucrose compounds is carried out in the process of liming and carbonatation and subsequent filtration. However, these operations involve high energy costs along with environmental pollution. For these reasons, many different clarification techniques, including electroclarification has been intensively investigated and applied. Juices and syrups formed during sugar cane processing contain compounds that impart yellow or brown colour to the white sugar. The coloured compounds are polymers with different molecular weights, structures and properties. These compounds are formed in the process as a result of sugar degradation reactions, pH changes, thermal effects and reactions between amino compounds and carbohydrates (Bento and S, 1998). These impurities may be occluded within sugar crystals, causing a negative effect on both the quantity and quality of the white sugar. Therefore, colour formation constitutes a challenging problem in sugar industry.

Colorants in sugar cane originate from two main sources: the sugar cane and the sugar refining process. Each sugar cane colorant is placed into one of four descriptive groups:

1) phenolics and flavonoids,
2) caramels,
3) melanoidins, and
4) alkaline degradation products of sucrose. In addition to these four groups, there are also colours precursors that do not themselves exhibit colour but will react with another non-coloured compound to form a coloured compound under favorable reaction conditions. Examples of these are amino acids, hydroxy acids, aldehydes, iron, and reducing sugars (Clarke et al., 1985; Carpenter, 1985).

The phenolics and flavonoids exist as glycosides attached to sugar residues (Clarke et al., 1985; Colombo et al., 2006). Some phenolics are not coloured when they first come from the plant, but oxidize, form complexes, or react to form colorants during processing. Molecules having other chemical groups develop colour during the refining process. These include caramels, melanoidins, and alkaline degradation products of the fructose moiety of sucrose. Caramels are known to originate from thermal degradation of glucose, while melanoidins are formed through the Maillard reaction involving amino compounds and the alcoholic hydroxyl groups on the sugars. Phenolic compounds in sugar cane

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juice that have been identified and quantified show the predominance of flavones, in a total content of around 160 mg/l (Colombo et al., 2005). Moreover, iron solubilized in juices may form chelates with anthocyanins, as with most of phenolic compounds, forming dark colour compounds (Paton and Smith, 1985). This reaction may happen whenever sugar solutions are in contact with iron, particularly during sugar extraction in mills. During cane milling there is an erosion of the rollers with iron passing to the juice.

The electroclarification of sugar cane juice is used to remove its non-sugar components specially coloured substances. It has advantages compared with chemical or biological methods. This electrochemical method has little or no harmful effects on the environment. This is because their techniques do not involve the use of harmful reagents. Thus, in this contribution, an attempt for testing the electroclarification of sugar cane juice using the protected aluminium electrodes coated with polyaniline/phosphate layer is investigated. The results obtained provide strong evidence on the possibility of developing a new and facile electrochemical approach to be used for sugar clarification.

The main objective of the present study is to investigate the optimum experimental parameters and conditions that could lead to an efficient electroclarification of sugar cane juice to produce sugar with high quality. This is achieved via using of a cheap aluminium alloy, Al1050, as working electrodes in the reactor cell. These electrodes are protected against corrosion through electrodeposition of a polyaniline/phosphate layer on the surface.

**Materials and methods**

**Cell and electrodes**

All chemicals are of Analytical Reagent, AR grade. Aniline is purified by vacuum distillation over zinc dust in order to eliminate the oxidative impurities. The purified aniline is always stored in dark. Disodium hydrogen phosphate, sodium dihydrogen phosphate, sodium hydroxide and sodium perchlorate (Merck) are used after purification. The phosphate buffer solutions are prepared by dissolving an appropriate amount of disodium hydrogen phosphate and sodium dihydrogen phosphate in deionized water. The cane juice solution is freshly prepared by diluting 10.0 cm$^3$ of raw juice to 50.0 cm$^3$ by using the prepared phosphate buffer solution.

A Potentiostat/Galvanostat (EG&G model 263A) and a personal computer are used. M352 corrosion and M270 Electrochemical software from EG&G Princeton Applied Research are used for electrochemical experiments. A hydrometer and polarimeter are used for Brix and polarity determination, respectively. A scanning electron microscope (JEOL JSM-5300) is used for SEM measurements. A one-compartment polypropylene cell containing three electrodes is used for electrodeposition and corrosion studies. A three-compartment cell is used for the electroclarification of sugar cane juice experiments.

Aluminium alloy 1050 is used as the working electrode for electrodeposition of polyaniline and the coated ones are employed for the electroclarification of the sugar cane juice. The alloy is specified as Al1050 according to the ASTM-Standard (Bayer & Gall, 1985) and obtained from Egyptalum Company, Egypt. The nominal composition is reported in Table 1. Samples of 10 x 50 x 1 mm are cut from the aluminium coupons. Samples are masked with adhesive tape at one end to get an effective working area of 3.3 cm$^2$. Prior to electrodeposition experiments, the samples are polished to a smooth surface finish, using successively fine (0.5 µm) grades of SiC paper and washed with deionised water.

Saturated calomel electrode (SCE) is used as the reference electrode. Two platinum foils are used as counter electrodes in electrodeposition measurements. However, only one platinum basket electrode is used in the electroclarification of sugar cane experiments as counter electrode.

**Table 1. Chemical composition (wt %) of aluminium alloy Al1050**

<table>
<thead>
<tr>
<th></th>
<th>Si</th>
<th>Fe</th>
<th>Mg</th>
<th>Mn</th>
<th>Cr</th>
<th>Cu</th>
<th>Ni</th>
<th>Ti</th>
<th>V</th>
<th>Zn</th>
<th>Others</th>
<th>Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>Composition (wt.%)</td>
<td>*0.25</td>
<td>*0.40</td>
<td>*0.05</td>
<td>*0.05</td>
<td>–</td>
<td>*0.05</td>
<td>–</td>
<td>*0.03</td>
<td>*0.05</td>
<td>*0.05</td>
<td>0.03</td>
<td>Min</td>
</tr>
<tr>
<td>Al1050</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>99.50</td>
</tr>
</tbody>
</table>
Preparation of polyaniline/phosphate coated aluminium alloy Al1050: Preparation of polyaniline/phosphate is carried out in aqueous solution containing 0.20 mol dm$^{-3}$ aniline/0.50 mol dm$^{-3}$ phosphate buffer (pH 5.0) at room temperature for all syntheses. After formation of the polyaniline/phosphate film on the surface of the aluminium alloy Al1050, the building solution is removed and the electrode is rinsed several times with deionized water.

Corrosion Studies on Polyaniline/Phosphate Coated Aluminium Alloy Al1050 in NaClO$_4$ solution: The potentiodynamic anodic polarization curves are recorded upon scanning the electrode potential, including compensation for the ohmic drop potential of the solution, automatically from $-1.15$ volt (more negative than the corrosion potential) up to 0.20 volt with scanning rate of 1.0 mVs$^{-1}$ at 298 K. The anodic polarization curves are recorded as log current density (log j) against potential (E), after allowing the electrode to reach the corrosion potential ($E_{corr}$) for a period of 1.0 hour immersed in 0.50 mol l$^{-1}$ NaClO$_4$ solution. Tafel analyses are performed on the aluminium alloy Al1050 electrode by polarizing the potential about 300 mV anodically and cathodically from the corrosion potential, $E_{corr}$, in 0.50 mol l$^{-1}$ NaClO$_4$ solutions. The resulting current is plotted on a logarithmic scale against potential.

Corrosion Studies on Polyaniline/Phosphate Coated Aluminium Alloy Al1050 in Sugar Cane Juice: The potentiodynamic anodic polarization curves are recorded on scanning the electrode potential from -0.70 volt (more negative than the corrosion potential) up to 0.00 volt with scan rate of 1.0 mVs$^{-1}$ at 298 K after allowing the electrode to reach the corrosion potential ($E_{corr}$) for a period of 1.0 hour in sugar cane juice (pH 7, 0.20 M phosphate buffer) solution. Tafel analyses are performed on polyaniline/phosphate coated aluminum alloy on polarizing the potential about 300 mV anodically and cathodically from the corrosion potential, $E_{corr}$, at scan rate of 1.0 mVs$^{-1}$ in sugar cane juice solution.

Cyclic Voltammetry of Sugar Cane Juice: Cyclic voltammetry of sugar cane juice at polyaniline/phosphate coated aluminium alloy electrode is performed for 50.0 cm$^3$ of juice solution (in 0.20 M phosphate buffer pH 7.0). The potential is scanning in the potential range from 0.0 to -1.1 volt at scan rate of 100 mV s$^{-1}$ at 298 K.

Square-Wave Voltammetry of Sugar Cane Juice: Square-wave voltammetry of sugar cane juice at polyaniline/phosphate coated aluminum alloy electrode is conducted for 50.0 cm$^3$ juice solution (in 0.20 M phosphate buffer pH 7.0). The voltammograms are recorded in the potential range from initial potential of -0.8 to 0.0 volt at frequency of 50 Hz.

Controlled Potential Coulometry of Sugar Cane Juice

The controlled-potential electrolysis of sugar cane juice is carried out in 0.20 M phosphate buffer solution, pH 7.0, by applying a constant potential of -0.51 volt on the polyaniline/phosphate coated aluminium alloy electrode at 298 K.

Analytical procedures of Sugar Cane Juice: Brix: Brix unit is commonly used in the sugar industry. It is defined as, the percent of the total dry substances dissolved in the sugar cane juice. The Brix is determined in volumetric Brix = (g/cm$^3$) % or gravimetric Brix = (g/g) %. The Brix is determined by using Hydrometer. Herein, Brix is the gravimetric Brix. Absorbance: The absorbance of sugar cane juice is determined by using JENWAY 6405 UV/VIS Spectrophotometer at $\lambda_{max}$ of 420 nm. Colour: Colour of the juice samples are calculated using ICUMSA method (ICUMSA method, 1994). International Commission for Uniform methods of Sugar AnalysisNorwich, UK.

\[
Colour = \frac{A \times 100000}{C_x l}
\]

where A is the absorbance at 420 nm, Cx is concentration (g/100ml), and l is cell width (cm).

\[
Decolourisation(\%) = 100 \times \left(1 - \frac{\text{colour cane juice}}{\text{colour sugar cane juice}}\right)
\]
Purity(%): Purity was defined according to Ghosh and Balakrishnan (Ghosh et al., 2000).

\[
Purity(\%) = 100 \times \left( \frac{\text{polarization}}{\text{brix}} \right)
\]

Polarity: The polarity of sugar cane juice is determined by using the polarimeter. The normal gravity of the polarimeter is 26. The juice is treated with 30% Pb(CH₃COO)₂, filtrated off and then the sample polarity is measured. Polarity = polarization value from the polarimeter.

Sugar(%): Sugar (%) = polarity × 1.04
Where, 1.04 is constant for the polarimeter.

Determination of Aluminum(III) traces in the sugar cane juice: Aluminum ions, Al(III) concentration in cane juice electrolyte before and after electro-clarification processes is traced by stripping voltammetric measurements (Vukomanvic et al., 1991). Aqueous sugar cane juice samples are analysed in 0.1 M acetate buffer (pH 6.5) mixed with 20 µM pyrocatechol violet (PCV). The pH adjustment is made on drop-wise addition of 0.1M acetate buffer solutions to the sample as required. Standard addition method is used for analysis.

Results and Discussion

Preparation of polyaniline/phosphate coated aluminium alloy Al1050

Synthesis of polyaniline/phosphate aluminum alloy Al1050 modified electrode is performed by potentiostatic techniques. The potentiostatic j-t transient for polyaniline deposition on aluminum alloy Al1050 electrode at an applied potential of 1.55 V for a period of 30 min is shown in Figure 1. As can be seen from Figure 1, the current drops sharply at the beginning due to the electrodeposition of the aniline monomer, then, the current is increased thereby reflecting the formation of aluminum phosphate. Finally, the current is decreased, reaching steady state at time of 1250 s as a result of formation of a polyaniline polymer on the aluminum substrate. Similar observations have been reported during electropolymerization of aniline from oxalic acid bath using steel or aluminum electrodes (Yagan et al., 2005; Karpagam et al., 2008).

SEM monitoring of the electrodeposition of polyaniline/phosphate films on aluminium alloy Al1050

The morphology of the uncoated and the polyaniline/phosphate coated aluminum alloy Al1050 is determined by scanning electron microscopy (SEM) as shown in Figure 2. The SEM micrograph of the polished uncoated electrode shows clearly the fine polishing groves on the surface (see Figure 2A).

![Figure 1. Potentiostatic response of aluminium alloy Al1050 electrode recorded during the synthesis of polyaniline/phosphate film in 0.50 M phosphate buffer (pH 5) containing 0.20 M aniline at 1.55 V.](image)

On electrodeposition of the polyaniline/phosphate layer, these groves disappear and a new texture is appeared as seen in Figure 2B and 2C. Figure 2D shows the morphology of the separate line between the coated and uncoated electrode surface. Taken together, these SEM images clearly suggest that the disappearance of the groves on the aluminium surface is due to formation of the polyaniline/phosphate layer on the surface.
Corrosion Studies on Polyaniline/Phosphate Coated Aluminum Alloy Al1050 in NaClO4 solution

Potentiodynamic Anodic Polarization Scan: Potentiodynamic anodic polarization curves recorded for uncoated and the polyaniline/phosphate coated aluminium alloy Al1050 in 0.50 M NaClO4 are shown in Figure 3. The potentiodynamogram for the uncoated electrode shows corrosion potential at -1.05 V, with an average current of 5.01 µA cm⁻², while the coated electrode shows a remarkable potential shift to noble values, -0.690 volt, with an average current of 1.2 µA cm⁻². The breakdown or pitting potential of the two electrodes is found to be -0.31 and -0.12 volts for the uncoated and coated electrodes, respectively. This behaviour clearly indicates that polyaniline/phosphate coating successfully protects the aluminium alloy Al1050 from corrosion in NaClO4 solution.

Figure 3. Potentiodynamic anodic polarization curves of uncoated and polyaniline/phosphate coated aluminium alloy Al1050 in 0.50 M NaClO4 at scan rate of 1.0 mV s⁻¹ and at 298 K.
Tafel Polarization Studies: Figure 4 shows the potentiodynamic polarization responses, known as Tafel curves, for uncoated and polyaniline/phosphate coated aluminum alloy Al1050 electrode obtained in 0.50 M NaClO₄ medium. The corrosion potential of the coated substrate (Ecorr = -0.683 V) is shifted 367 mV more anodic compared to that of the uncoated one (Ecorr = -1.05 V). Moreover, the corrosion current, Jcorr = 0.26 µA/cm² decreases on coating the substrate electrode with polyaniline/phosphate compared that of uncoated one, Jcorr = 43.0 µA/cm² (c.f. Table 2).

Figure 4. Tafel curves obtained for uncoated and modified aluminum alloy Al1050 electrode in 0.50 M NaClO₄ solution at 298 K.

Table 2. Corrosion potential, corrosion current, corrosion rates and Tafel slopes obtained for coated and uncoated aluminum alloy Al1050 in 0.5 M NaClO₄ solution.

<table>
<thead>
<tr>
<th>Electrode Type</th>
<th>Ecorr (V SCE)</th>
<th>Jcorr (µA/cm²)</th>
<th>Corrosion rate (mpy)</th>
<th>Bₐ (V/decade)</th>
<th>Bₘ (V/decade)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Uncoated Al1050</td>
<td>1.05</td>
<td>43.00</td>
<td>18.80</td>
<td>0.70</td>
<td>0.10</td>
</tr>
<tr>
<td>Modified Al1050</td>
<td>0.623</td>
<td>0.24</td>
<td>0.11</td>
<td>0.38</td>
<td>0.09</td>
</tr>
</tbody>
</table>

The potentiodynamogram shows also that, the anodic and the cathodic currents for the coated substrate are very low compared to that for uncoated one. Table 2 summarizes the corrosion current densities (Jcorr) obtained by extrapolating the linear portions of the Tafel plots. Taken together, the combined results of Tafel Polarization Studies for the uncoated and polyaniline/phosphate coated aluminum alloy Al1050 electrode clearly establish that corrosion current, Jcorr, corrosion potential, Ecorr, and the corrosion rate decrease significantly when polyaniline is electrodeposited on aluminum alloy Al1050 electrode surface. This reveals that the polyaniline/phosphate layer restricts the anodic and the cathodic reactions of the subject alloy in aggressive media, consequently, decreases the susceptibility of the aluminum alloy to pitting corrosion (MacDiarmind et al., 1987).

In that context, the protection efficiency (PE%) for polyaniline/phosphate is calculated by using the following expression: PE % = [(Rₚc – Rₚ)/Rₚc] x 100
where Rₚ and Rₚc denote the polarization resistance of the uncoated and polyaniline/phosphate coated aluminum alloy, respectively. In addition, the polarization resistances, Rₚ and Rₚc are estimated from the Tafel plots, according to the Stern–Geary equation (Stern and Geary, 1957) given as,

\[ R_p = \frac{b_a b_c}{2.303(b_a + b_c)J_{corr}} \]
Here, \( J_{\text{corr}} \) is the corrosion current determined by an intersection of the linear portions of the anodic and cathodic curves, and \( b_a \) and \( b_c \) are the anodic and cathodic Tafel slopes, respectively. The PE\% calculated from potentiodynamic polarization data is found to be \( \sim 99.2\% \). This supports the capability of polyaniline to act as a corrosion protective layer on aluminum alloy.

It worth noting that polyaniline/phosphate has several oxidation states (MacDiarmid et al., 1987). The most stable and the only conductive form of these is the emeraldine base (EB). It has equal amounts of reduced and oxidized repeating units and the basic form of emeraldine base can be represented as follow:

\[
y = 0.5.
\]

Moreover, Corrosion protection by polyaniline/phosphate coating on aluminum alloy could be related to its capability to decrease the rate of oxygen and proton cathodic reactions on the substrate by its barrier properties (Wen and Kocherginsky, 1999) However, potentiodynamic polarization studies show an anodic shift of the corrosion potential and low cathodic current (c.f. Figure 4). This suggests some electrochemical activity of the polyaniline coating. Thus, polyaniline is expected to give rise to a galvanic coupling with aluminum, due to its more positive redox potential (Cogan et al., 2000).

**Corrosion Studies of polyaniline/phosphate coated Aluminum Alloy Electrodes in Sugar cane Juice**

Figure 5 shows a typical potentiodynamic anodic polarization curves recorded for polyaniline/phosphate coated aluminium alloy electrode in 0.50 M NaClO\(_4\) and in sugar cane juice solutions (pH 7, 0.20 M phosphate buffer). As can be seen from Fig. 5, the corrosion potential \( (E_{\text{corr}}) = -0.595 \text{ volt} \), and pitting potential \( (E_{\text{pit}}) = -0.08 \text{ volts} \) are nobler than the corrosion potential \( (E_{\text{corr}}) = -0.69 \text{ volt} \), and pitting potential \( (E_{\text{pit}}) = -0.12 \text{ volts} \) for the uncoated electrode in NaClO\(_4\) solution. In addition, Tafel Polarization Study, Figure 6, verified this protection behaviour, since the corrosion potential of the coated substrate in cane juice solution \( (E_{\text{corr}} = -0.595 \text{ V}) \) is shifted 95 mV to more anodic direction compared to that of in perchlorate medium \( (E_{\text{corr}} = -0.690 \text{ V}) \). Similarly, the corrosion current \( (j_{\text{corr}} = 0.19 \mu \text{A/cm}^2) \) in cane juice solution is lower than that for perchlorate medium \( (j_{\text{corr}} = 3.16 \mu \text{A/cm}^2) \), c.f. Table 3. These results suggest that the coated aluminium electrode is suitable for the electroclarification of sugar cane juice.

![Figure 5](image-url)

**Figure 5.** Potentiodynamic anodic polarization curves of polyaniline/phosphate coated aluminium alloy in 0.50 M NaClO\(_4\) and in sugar cane juice solution (pH 7.0, 0.20 M phosphate buffer) at a scan rate of 1.0 mV s\(^{-1}\) and at 298 K.
Figure 6. Tafel curves obtained for polyaniline/phosphate coated aluminum alloy in 0.50 M NaClO₄ and in sugar cane juice solutions (pH 7, 0.20 M phosphate buffer) at a scan rate of 1.0 mV s⁻¹ and at 298 K.

Cyclic Voltammetry of Sugar Cane Juice

The bulk electrolysis of the sugar cane juice by controlled-potential electrolysis must be performed at constant potential. The electrolysis potential is determined by cyclic voltammetry of sugar cane juice on coated polyaniline/phosphate aluminum alloy Al1050 electrode.

Cyclic voltammograms, cv, of sugar cane juice at coated polyaniline/phosphate aluminum alloy electrode is performed in 0.20 M phosphate buffer solution at pH 7.0 as shown in figure 7. Upon scanning the potential from the initial value of 0.0 volt to more negative, no current response is observed. This indicates the absence of any reduction processes of the sugar cane juice colorants, Vola, on the forward scan. However, on switching the scan at a potential value of -1.1 volt and sweeping the potential towards the positive direction, the voltammogram shows an irreversible oxidation cv wave with a peak potential at -0.51 volt versus SCE at scan rate of 100 mV/sec. This behaviour can be rationalized via Scheme 1

\[
\text{Vola} \leftrightarrow \text{Vola}^{2+} + 2e^- \\
\text{Vola}^{2+} + 2X^- \leftrightarrow \text{VolaX}_2 \text{(the final product)}
\]

Scheme 1

Where, Vola is the coloured substance in the cane juice. According to Scheme 1, in the forward scan, the Vola, at the electrode surface is electroinactive. Thus, no reduction response for it is seen.

Figure 7. Cyclic voltammogram of sugar cane juice on coated polyaniline/phosphate aluminum alloy electrode in 0.20 M phosphate buffer solution at scan rate of 100 mV s⁻¹ and at 298 K.
Upon switching the scan direction and sweeping toward the positive voltage, the substrate, Vola, is electroactive and undergoes oxidation. Similar redox behavior was reported earlier (Ravanel et al., 1986; Deriglazov et al., 1978; Rapta et al., 1995). This behavior is further supported by square-wave voltammograms (Figure 8) obtained for the sugar cane juice at the coated polyaniline/phosphate aluminium alloy electrode under the same condition as in Figure 7, which shows a strong oxidation peak at -0.51 volt. It is worth noting that this peak falls in the passivation region of the coated polyaniline/phosphate aluminum alloy electrode. Accordingly, the controlled-potential electrolysis, see below, is performed at that value (i.e., -0.51 V).

**Figure 8.** Square-wave voltammogram of sugar cane juice on coated polyaniline/phosphate aluminium alloy electrode in 0.20 M phosphate buffer, pH 7.

**Table 3.** Corrosion potential, corrosion current, corrosion rates and Tafel slopes obtained for polyaniline/phosphate coated aluminium alloy in 0.50 M NaClO4 and in cane juice solutions.

<table>
<thead>
<tr>
<th>Solution</th>
<th>(-E_{\text{corr}}) V, SCE</th>
<th>(I_{\text{corr}}) ((\mu)A/cm(^2))</th>
<th>Corrosion rate (mpy)</th>
<th>(b_2) (V/decade)</th>
<th>(b_3) (V/decade)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaClO(_4)</td>
<td>0.690</td>
<td>3.160</td>
<td>1.400</td>
<td>0.650</td>
<td>0.900</td>
</tr>
<tr>
<td>Sugar cane juice</td>
<td>0.595</td>
<td>0.190</td>
<td>0.080</td>
<td>0.360</td>
<td>0.080</td>
</tr>
</tbody>
</table>

**Controlled potential electrolysis of sugar cane juice**

In order to electrolyse the entire solution rather than the thin layer at the vicinity of the electrode surface when either CV or SWV techniques are used, controlled-potential electrolysis experiments of sugar cane juice were conducted in 0.20 M phosphate buffer solution, pH 7.0 and at a constant applied potential of -0.51 volt, using the coated polyaniline/phosphate aluminium alloy electrodes at 298 K. It is clear from Figure 9 that the current decays exponentially with time during the electrolysis and eventually reaches the background (residual) current level within 20 minutes of electrolysis.

This means that sugar cane juice is completely electrolyzed upon the passage of current for 20 minutes. However, many other experimental parameters such as pH of the solution, electrolysis time, applied potential, working electrode area, temperature, and supporting electrolyte concentration are believed to play crucial role in the efficiency of the electroclarification process as will be elaborated in details below.
**Effect of the pH on the electrolysis of sugar cane juice**

Figure 10 shows the effect of pH (range = 4-10) on the colour of the electrolyzed juice at applied potential of -0.51 volt for 20 min of electrolysis at working electrode having a surface area of 4.0 cm². The colour is measured at the sugar cane juice maximum colour signal of 417 nm. From the figure 10, it clear that, the minimum colour value for the electrolysis process is found at pH 7.0. Thus, it is concluded that, the effective pH for the electrolysis process is 7.0.

**Figure 10.** Effect of pH on the colour of electrolyzed sugar cane juice solution at applied potential of -0.51 Volt for 20 min with 4.0 cm² working electrode area.

(ii)-**Effect of the time on the electrolysis of sugar cane juice:**

The effect of electrolysis time is investigated for the juice at pH 7.0 and applied electrolysis potential of -0.51 volt. The working electrode area is 4.0 cm². The data obtained are illustrated in Figure 11. Examination of the obtained data reveals that within 20 min of electrolysis the generated current reaches a very low level (background current), thereby indicating that 20 min of electrolysis time is sufficient to decolourise the entire sample solution of the sugar can juice.
Effect of electrolysis time on the colour of cane juice solution, pH 7.0 at applied potential of -0.51 volt with working electrode area of 4.0 cm².

Effect of the electrode surface area on the electrolysis of sugar cane juice

The electrolysis of sugar cane juice is investigated for the juice solution (pH = 7.0) at different electrode surface area at applied electrolysis potential of -0.51 volt for 20 min. The data obtained are plotted in Figure 12. On examination of these data, it is clear that, the colour intensity of the tested sugar cane juice solution, 20.0 cm³ volume, decreases on increasing the surface area of the working electrode. At working electrode surface area of ≥ 3.3 cm² the colour intensity of the juice solution reaches the lowest level.

Effect of the heating on the sugar cane juice before electrolysis

Figure 13 shows the effect of temperature on sugar cane juice colorants. From that figure, it can be seen that the optimum temperature for heating the juice before the electrolysis is 36.5 °C at constant heating time 10 minutes, then the electrolysis process is performed at room temperature. However, To determine the optimum heating time of the juice before electrolysis, the heating is performed at different time intervals. Figure 14 shows the effect of heating time at a constant
temperature of 36.5 °C on the colour of sugar cane juice. It is revealed that, the colour remains constant nearly after 40 minutes of heating.

![Figure 13](image1.png)

**Figure 13.** Effect of temperature on the colour of cane juice, pH 7.0, at applied potential of -0.51 volt for 20 min and electrode surface area of 3.3 cm².

![Figure 14](image2.png)

**Figure 14.** Effect of the heating time at temperature 36.5 °C on the colour of cane juice, pH 7.0, at applied potential of -0.51 volt for 20 min and electrode surface area of 3.3 cm².

**Effect of phosphate concentration on the electrolysis of sugar cane juice**

The effect of phosphate concentration on the electroclarification of raw sugar cane juice is conducted via addition of different concentrations of the buffer. The electrolysis is performed at constant pH (7.0), applied potential of -0.51 volt for 20 minutes and electrode surface area of 3.3 cm². The data obtained are recorded in colour of the sugar cane juice against the concentration of phosphate buffer. Figure 15 shows the dependence of the juice colour intensity on the concentration of phosphate from over the range from 0.0 to 0.2 M.

![Figure 15](image3.png)
Figure 15. Effect of the phosphate concentration on the colour of sugarcane juice, at pH 7.0, applied potential of -0.51 volt for 20 min and electrode surface area of 3.3 cm².

Taken together, the combined finding of the above mentioned experimental parameters clearly demonstrate that the optimum conditions for the electroclarification of the sugar cane juice are electrolysis potential of -0.51 volt and 20 min electrolysis time with stirring at pH 7.0 and 0.05 M phosphate concentration after heating the juice at 36.5°C for 40 minuets.

Table 4. Analytical data of sugarcane juice before and after the electro-clarification process

<table>
<thead>
<tr>
<th></th>
<th>Brix</th>
<th>Colour</th>
<th>Polarity</th>
<th>Sugar %</th>
<th>Purity %</th>
<th>Aluminium traces</th>
</tr>
</thead>
<tbody>
<tr>
<td>Before</td>
<td>16.45</td>
<td>1033.4</td>
<td>13.52</td>
<td>14.06</td>
<td>85.47</td>
<td>---</td>
</tr>
<tr>
<td>After Scale minimisation</td>
<td>16.35</td>
<td>941.9</td>
<td>13.48</td>
<td>14.02</td>
<td>85.75</td>
<td>---</td>
</tr>
<tr>
<td>After electrolysis</td>
<td>16.22</td>
<td>647.3</td>
<td>13.5</td>
<td>14.04</td>
<td>86.56</td>
<td>---</td>
</tr>
<tr>
<td>Removal %</td>
<td>1.40</td>
<td>---</td>
<td>0.15</td>
<td>0.14</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>Decolourisation %</td>
<td>---</td>
<td>37.40</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
</tbody>
</table>

Moreover, the electroclarification of sugar cane juice is performed using the coated polyaniline/phosphate aluminium electrodes at the above mentioned optimum conditions. Data obtained are compared with that for the raw juice. Table 4 shows the efficiency of the present electroclarification of sugar cane juice. According to these data, it is revealed that, after heating the juice at 36.5°C for 40 minuets, Brix and colour are minimized and the sugar percentage is more or less has a constant value. Thus, after electrolysis process, the colour intensity is minimized while the sugar percentage and the purity remain unchanged. Accordingly, electroclarification process has high efficiency for removal of about 37.40 % of the colorants, 1.40 % of Brix and provided total sugar purity of about 85.47%. More importantly, the process has no harmful effect on the sugar content, which is found to be 14.06% and 14.04% for the raw and clarified juice, respectively. This is the most important component in sugar cane industry. Furthermore, no dissolution of the used aluminium electrodes in the sugar cane juice electrolyte is observed. Finally, and most importantly from industrial health viewpoints is that the present electroclarification of sugar cane juice is performed without usage of hazardous chemicals. Therefore, via this new approach, we provide energy efficient and
environmentally friendly process for production of refined sugar with superior quality. The process is may consider to be a direct replacement of the conventional clarification processes for sugar productions.

Conclusion

The findings of this research have shown that corrosion protection by polyaniline/phosphate coating on aluminium alloy Al1050 could be related to its capability to decrease the rate of oxygen and proton cathodic reactions on the aluminium substrate by its barrier properties. The electroclarification of sugar cane juice is performed using the polyaniline/phosphate coated aluminium Al1050 electrodes at the estimated optimum conditions. The electroclarification process has high efficiency by removal of 37.40 % of sugar colorants, 1.40 % of Brix and produce 85.47% pure sugar. The process could be utilized in the future to replace the conventional clarification methods widely used in sugar industry.

Acknowledgment: The authors gratefully acknowledge Prof. Hossam El-Din Abdel-Ghany, chairman of the Chemistry Department, Faculty of Science, Sohag University for his help and support. This work is a partial fulfilment of the requirements for a Masters degree in Science for one of us (Emad Newair) and was totally funded and conducted at Sohag University.

References


The Air Pollution from the Port-Piri Furnace’s Gases

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Abstract. The paper has as a studying object the issue of effective management of gasses’ heating and dusts in reductive melting process in lead (Pb) metallurgy. It also analyses the issue related to the usage and recycling of dusts and gasses in all pyro-metallurgical processes of technical lead production. The paper contains the analysis of technological process of separation of humidity, gasses, and dusts of valuable remainders in “Trepça” plant. Paper has the results of theoretical-experimental studying, analytical and graphical of gasses thermal balance depending on height and composition of load, and the coke quantity on load for reductive melt in “Water-Jacket” furnaces. With thermal balance, having into consideration all parameters of heat in entry and exit depending on aforementioned factors we aimed to optimize the parameters of the process, keeping the attention to the minimization of energy consumption, and the overall influence on environment.

Keywords: load, coke, heat, humidity, dusts, gasses, environment.

Introduction

The upper part of the furnace which is the study point of this paper lies from the reactions zone of Water-Jacket furnace and it also includes the furnace neck. In this zone has been elaborated the zonal material balance referenced third in the row. The separation of humidity, dusts, gases and load with gases depends on many parameters like temperature, load composition, and height of load inserted in the furnace, and also the height the height of preheating zone in Water-jacket furnace. Lead oxidizes in reaction zone of the furnace and exhales with gases like dusts and small particles after which falls in worthy storage of Trepça plant and has negative effects in environment, and economic stability of reductive melting process of Water-jacket furnace.

Thermal balance of gases in this zone depends on many factors; height and load composition, coke quantity in a load. The calculation has been done as the standard methodology of thermal calculation is done; moreover, by using a computer for mathematical models which enables very accurate results. We must emphasize that acquired and used heat in reaction zone and melted materials is calculated in others studies, so their influence in preheating zone is assumed.

The Calculation of Thermal Balance in Preheating Zone of Water-Jacket Furnace

The thermal balance in preheating zone in Water-jacket furnace consists of acquired heat which can be variable and depends on the chemical composition of load, agglomerate and reductive-oxidative features of agglomerate. Simultaneously, thermal balance in preheating zone consists of used heat which also can be variable and depends on load height inserted for reductive melt, the quantity of coke inserted in furnace and the quantity of formed gases. These gases are exhaled in the atmosphere from the reductive melting process in Water-jacket furnace.

Acquired Heat

a) The heat that enters with agglomerate which is taken resources is calculated with formula:

\[ Q_{agl} = G_{agl} \cdot C_{agl} \cdot t_{agl} (kJ / h) \]

Abbreviations of which are:

\( G_{agl} \) - agglomerate weight \((22250 kg / h)\),

\( C_{agl} \) - specific heat of agglomerate \((0.120 kJ / kg^{\circ}C)\),

\( t_{agl} \) - agglomerate temperature \((25^{\circ}C)\),

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The heat that enters with agglomerate which immediately is inserted in furnace from the agglomeration machine type of Dwight Lloyd or Lurgi is calculated with formula:

\[ Q_{\text{agl}} = G_{\text{agl}} \cdot C_{\text{agl}} \cdot t_{\text{agl}} \left( \frac{kJ}{h} \right) \]

Abbreviations of which are:
- \( G_{\text{agl}} \) - agglomerate weight \((22250 \text{ kg} / h)\),
- \( C_{\text{agl}} \) - specific heat of agglomerate \((0.120 \text{ kJ} / \text{kg} \cdot ^\circ \text{C})\),
- \( t_{\text{agl}} \) - agglomerate temperature \((50^\circ \text{C})\)

The table below shows acquired heat with agglomerate which depends on agglomerate temperature.

**Table 1. The acquired heat with agglomerate depending on agglomerate temperature**

<table>
<thead>
<tr>
<th>Agglomerate temperature (^{\circ} \text{C} )</th>
<th>Agglomerate quantity ( \text{kg} / h )</th>
<th>Specific heat of agglomerate ( \text{kJ} / \text{kg} \cdot ^\circ \text{C} )</th>
<th>Quantity of heat ( \text{kJ} / h )</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>22250</td>
<td>0.120</td>
<td>66750</td>
</tr>
<tr>
<td>50</td>
<td>22250</td>
<td>0.120</td>
<td>133500</td>
</tr>
</tbody>
</table>

**Figure 1.** The chart shows acquired heat from agglomerate depending on agglomerate temperature

**The Used Heat**

For the sake of having exact management of thermal gases in preheating zone the calculation of used heat is done by alternatives based on enthalpy values.

a) The usage of heat to boil the humidity from coke is calculated with formula:

\[ Q^{H_2O} = i^{H_2O} \cdot V \left( \frac{kJ}{h} \right) \]

\[ i^{H_2O} = C_p^{H_2O} \cdot t \left( \frac{kJ}{m^3} \right) \]

- \( i^{H_2O} \) - the enthalpy of steam,
- \( C_p^{H_2O} \) - specific heat of steam \((1.56 \text{ kJ} / \text{m}^3 \cdot ^\circ \text{C})\),
- \( t \) - the separation temperature of crystal water,

\[ i^{H_2O} = 626.2 \text{ kJ} / \text{m}^3 \]

\[ Q^{H_2O} = i^{H_2O} \cdot V \left( \frac{kJ}{h} \right) \]

\( V \) - the quantity of humidity in a kilogram coke is calculated with formula:

\[ V = R'_i - R_i \left( \frac{m^3}{kg} \right) \]
$R'_t$ - the theoretical quantity of wet gases calculated with Rumumel formula:

$$R'_t = 1.5 + 0.5 \frac{Q_f}{1000} \left( \text{m}^3/\text{kg} \right)$$

$Q_f$ - thermal power of coke.

$R'_t = 31.2 \text{ m}^3/\text{kg}$

$R_t$ - theoretical quantity of dry gases taken from diagram $J_t$ depending on $Q_f$ and $\lambda$.

$R_t = 12 \text{ m}^3/\text{kg}$

$V = 31.2 - 12 = 19.2 \text{ m}^3/\text{kg}_{\text{koks}}$

The table shows the quantity of humidity in coke and the value of used heat for boiling the humidity calculated with enthalpy.

**Table 2.** The quantity of humidity and the enthalpy for quantity of coke used

<table>
<thead>
<tr>
<th>Coke quantity (kg)</th>
<th>Quantity of humidity (m^3/kg)</th>
<th>Enthalpy (kJ/m^3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>19.2</td>
<td>626.2</td>
</tr>
<tr>
<td>2</td>
<td>36.4</td>
<td>1252.4</td>
</tr>
<tr>
<td>3</td>
<td>57.6</td>
<td>1878.6</td>
</tr>
<tr>
<td>1000</td>
<td>19200</td>
<td>626000</td>
</tr>
</tbody>
</table>

**Figure 2.** Graphical representation of coke quantity, humidity, and the value of heat usage calculated with enthalpy.

b) The loss of heat with gases is calculated with formula:

$$Q_{\text{gas}} = i_{\text{gas}} \cdot V (kJ/h)$$

$$i_{\text{gas}} = C_{p_{\text{gas}}} \cdot t_{\text{gas}} (kJ/m^3)$$

$i_{\text{gas}}$ - gases' enthalpy,

$C_{p_{\text{gas}}}$ - specific heat of gases $1.36 \text{ kJ/m}^3^\circ\text{C}$

$t_{\text{gas}}$ - gases' temperature on the exit of furnace neck which depends on many factors and has different values, in this case $300^\circ\text{C}$.

$$i_{\text{gas}} = 408 \text{ kJ/m}^3$$

The table below shows the enthalpy for gases depending on temperature of gases in the way out of furnace neck.
Table 3. The enthalpy of gases depending on temperature of gases

<table>
<thead>
<tr>
<th>Specific heat of gases (kJ/m³°C)</th>
<th>Temperature of gases (°C)</th>
<th>Enthalpy of gases (kJ/m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.36</td>
<td>300</td>
<td>408</td>
</tr>
<tr>
<td>1.36</td>
<td>400</td>
<td>544</td>
</tr>
<tr>
<td>1.36</td>
<td>450</td>
<td>612</td>
</tr>
<tr>
<td>1.36</td>
<td>500</td>
<td>680</td>
</tr>
</tbody>
</table>

Figure 3. The chart shows the enthalpy values depending on gases temperature

c) Volume of dry gases during coke burning is calculated proportionally as below:

\[
\begin{align*}
V &= \frac{2420 \text{kg}_\text{coke} \cdot 12 \text{ m}^3/\text{kg}_\text{coke}}{1 \text{ kg}_\text{coke}} \\
V &= 29040 \text{ m}^3/\text{kg}_\text{coke}
\end{align*}
\]

d) The quantity of water in coke is the humidity percentage in coke, if there is 10% humidity in coke then water quantity in coke will be:

\[
\begin{align*}
\text{m}_{H_2O} &= G_{\text{coke}} \cdot 10\% (\text{kg}/\text{h}) \\
\text{m}_{H_2O} &= 2420 \text{ kg}/\text{h} \cdot 0.1 \\
\text{m}_{H_2O} &= 242 \text{ kg}/\text{h}
\end{align*}
\]

Steam volume in gases is calculated proportionally as below:

\[
\begin{align*}
V &= \frac{2420 \text{kg}_\text{coke} \cdot 19.2 \text{ m}^3/\text{kg}_\text{coke}}{1 \text{ kg}_\text{coke}} \\
V &= 46464 \text{ m}^3/\text{kg}_\text{coke}
\end{align*}
\]

e) Heat loss for boiling humidity from coke is calculated with formula:

\[
\begin{align*}
Q_{H_2O}^{\text{H}_2O} &= i_{H_2O}^{\text{H}_2O} \cdot V (\text{kJ}/\text{h}) \\
Q_{H_2O}^{\text{H}_2O} &= 626.2 \cdot 46464 \text{kJ}/\text{h} \\
Q_{H_2O}^{\text{H}_2O} &= 29095756.8 \text{kJ}/\text{h}
\end{align*}
\]
Heat loss with gases is calculated with formula:

\[ Q_{\text{gas}} = i_{\text{gas}} \cdot V(kJ/h) \]

\[ Q_{\text{gas}} = 11848320 \, kJ/h \]

Table shows heat loss for boiling humidity from coke and heat loss with gases.

**Table 4. The heat loss with humidity and with gases**

<table>
<thead>
<tr>
<th>Component</th>
<th>Enthalpy ( (kJ/m^3) )</th>
<th>Volume of dry gases ( (m^3/kg) )</th>
<th>Volume of gases with steam ( (m^3/kg) )</th>
<th>Heat loss ( (kJ/h) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Boiling humidity from coke</td>
<td>626.2</td>
<td>46464</td>
<td>29040</td>
<td>29095756.8</td>
</tr>
<tr>
<td>With gases which exit furnace</td>
<td>408</td>
<td>29040</td>
<td>11848320</td>
<td></td>
</tr>
</tbody>
</table>

![Graphical representation of energy usage for boiling humidity from coke and for gases.](image)

**Table 5. The technologic indexes of melt with high and low pillar of load**

<table>
<thead>
<tr>
<th>Name</th>
<th>Unit</th>
<th>Melt with high pillar (5-6m)</th>
<th>Melt with low pillar (2.5-3m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Capacity</td>
<td>t/m²</td>
<td>45-60</td>
<td>60-75</td>
</tr>
<tr>
<td>Coke consumption</td>
<td>%</td>
<td>9-11</td>
<td>7.5-10</td>
</tr>
<tr>
<td>Pb quantity in sinter</td>
<td>%</td>
<td>Up to 1.5</td>
<td>3-3.5</td>
</tr>
<tr>
<td>Temperature of gases on furnace neck</td>
<td>°C</td>
<td>100-150</td>
<td>600</td>
</tr>
<tr>
<td>Air consumption</td>
<td>m³/t</td>
<td>900</td>
<td>1400</td>
</tr>
<tr>
<td>Quantity of dusts</td>
<td>%</td>
<td>0.5-1</td>
<td>3-5</td>
</tr>
</tbody>
</table>

Heat loss with gasses with low pillar of load for melt in Water-jacket furnace is calculated with:

\[ Q = R \cdot C_p \cdot t \cdot m(kJ/h) \]

- \( R \) - Quantity of gasses which exit the furnace \( (15.4 \, m^3/kg) \)
- \( C_p \) - Specific heat of gases \( (1.36 \,kJ/m^3) \)
t - Temperature of gases that exit the furnace \( (600^\circ C) \)

\( m \) - Consumed quantity of coke \( (2420 \text{ kg/h}) \)

\[ Q = 30410688 \text{kJ/h} \]

b) Heat loss with gases in high pillar of load for melt in Water-jacket furnace is calculated with formula:

\[ Q^U = R \cdot C_p \cdot t \cdot m \text{(kJ/h)} \]

\( R \) - Quantity of gases that exit the furnace \( (15.4 \text{ m}^3/\text{kg}) \),

\( C_p \) - Specific heat of gases \( (1.36 \text{kJ/m}^3) \),

\( t \) - Temperature of gases that exit the furnace \( (100^\circ C) \),

\( m \) - Consumed quantity of coke \( (2420 \text{ kg/h}) \),

\[ Q^U = 5068448 \text{kJ/h} \]

The table below shows heat loss with gases for high and low pillar of load.

**Table 6. The heat loss with gases for high and low pillar of load**

<table>
<thead>
<tr>
<th>Pillar of load</th>
<th>Quantity of coke consumed ( (\text{kg/h}) )</th>
<th>Gases temperature ( (^\circ C) )</th>
<th>Quantity of lost heat ( (\text{kJ/h}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low pillar</td>
<td>2420</td>
<td>600</td>
<td>30410688</td>
</tr>
<tr>
<td>High pillar</td>
<td>2420</td>
<td>100</td>
<td>5068448</td>
</tr>
</tbody>
</table>

**Figure 5.** Graphical representation of heat loss with high and low pillar of load for melt in Water-jacket furnace in “Trepça”

**Conclusion**

Having considered the calculation we can conclude that heat lost with gases has high values, in particular for melting process with low pillar of load in the furnace. Temperature of gases mainly depends on height of load and load composition for melt, quantity of consumed coke per ton technical lead produced in Water-jacket furnaces in Trepça.

Based on analytical and experimental calculation of thermal balance of gases in preheating zone of Water-jacket furnace we can argue that acquired energy (that enters the process) is minimal comparing to used energy.

Thus, this difference results in emission formation, dusts layers, and gases that convey heat and dusts on environment which pollute the environment and destabilize reductive melting process of agglomerate in Water-jacket furnace.

In conclusion, to reduce the emission formation, gases, dust layers, and loss of heat quantity with gases we should influence in:

- the enlargement of load height in furnace,
- exact consumption of coke per ton technical lead produced,
• load consumption for melt with minimal humidity, and
• exact consumption of air for coke burn.

References
The Determination of Deposited Dust and Heavy Metals in the Industrial Area of Ferronikeli Smelter

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Abstract: In this scientific paper is presented the determination of deposited dust (aerosediment) and heavy metals in dust from air monitoring in the industrial area of Ferronikeli smelter, located in the municipality of Drenas of the Republic of Kosovo. The Ferronikeli smelter is one well known industrial complex for production of commercial ferronickel and as result of technological process applied ranged in heavy industries, so from production process expected that from its chimneys to release in air dust and other polluted substances, as well as heavy metals. The results presented in this paper are based on monitoring of the environment during the year 2008, where are shown results from these measurements and analyses for the quantity of deposited dust (gravimetric method), as well as the determination of heavy metals in dust with atomic absorber spectrometer (AAS). Monitoring includes the industrial area where lies Ferronikeli smelter (some points inside of smelter area) and some other monitoring points in urban area of Drenas (outside from smelter). Based on these data, it is evident the impact of Ferronikeli smelter on the environment, especially with emphasis on air. Key words: deposited dust, heavy metals in dust, gravimetric method, X-Ray Fluorescence Spectrometry.

Introduction

The large natural resource of ores has contributed at industrial development, that is a major branch of developing of the municipality of Drenas and industrial development of Kosovo in general. Ferronikeli smelter is an existing metallurgical plant that produces commercial ferronickel as a final product. Ferronikeli has started with production in 1984 until 1999, when all activities are stopped. Ferronikeli has restarted with production again in 2007 after its privatizing.

The plant lies in a flat area with a slight slope from North-East to South-West, from 620 to 590 m. At the end of the slope located the Drenica River, running towards East at 1 km from the South boundary of the area, at a level of 570 m.

Monitoring of deposited dust

The main influence in ambient air from Ferronikeli smelter coming from: rotary kiln stack, electric furnaces stacks and the stack of converter. As a result of technological process applied for ferronickel production, these substances expected to discharge in ambient air: solid particulates (dust), sulphur dioxide (SO₂), nitrogen oxides (NOx), carbon dioxide (CO₂) and carbon monoxide (CO).

Considering these conditions, is needed to perform the measurements of these substances mentioned above and proceedings with treatment of air pollution problems with dust and the other substances in Ferronikeli complex and its influence in the area of the municipality of Drenas and surroundings, in the view of monitoring system in several measurement points and the available data from direct measurements.

Principle of the method

Large solid and liquid particles (with aerodynamic diameter >10 nm) collect by gravity into a storage container with open hole after a certain period of time. The vessel washed with a known amount of distilled water, which filtered and then evaporates. The mass of insoluble particles determine by weight difference after evaporation. These weight differences express total content of

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deposited particles from the air; soluble and insoluble their parts. Deposition period and collection surface are important parameters. Soluble and insoluble particles are subject of further analysis for elements, inorganic and organic compounds.

**Interferences - obstacles**

Not considering part of the deposited particles excrement of birds, insects, algae and big pieces of plants. Excrement birds minimized through a circle for their stand. In solution of collection vessel could be added algaecide and fungicide. Particles with diameter greater than 1 mm remove through a sieve.

Sampling efficiency of cylindrical vessels is almost zero for wind speeds greater than 7 m/s for particles of order 100 μm. Efficiency is about 60% for 100 nm particles, wind speed 1 m/s. Dry particles collected in a vessel can re-suspend of wind further. A quantity of water in the vessel minimizes this kind of interference.

**Description of the equipment for deposited dust**

The form of equipment for collecting dust is from metallic funnel (d=31.5 cm) and bottle (vessel) to collect dust and water. Construction should be placing in one open place and at high about 1.7m from ground level. Bottle has to be washed with detergent, rinsed with water and dried before placing. Equipment has to be positioned where there are no big trees or buildings.

**Sampling**

Equipment has to be sampled after 1 month (30 ± 2 days). If it rains a lot, change the bottle to avoid overflowing. Check the equipment (condition, water-level). Complete one sampling sheet. Wash down the funnel with 1/2L of water in order to collect the remaining dusts from the funnel. Remove the bottle and replace it with a clean one. Close the bottle with a cap when transported to the laboratory. Store the bottle in a dark place up to 14 days. Complete one diary during the monitoring.

**Materials and Methods**

**Analyses**

Leaves and insects have to be removed from the bottle. Sample has to be filtrated with a filter of 3 micrometers. If the sample is less than 150 mL or if there is no water, then add 150-200 mL of distillated water in the bottle. Evaporate water from the sample by placing it in a 105°C oven. At the end, place it in desiccators with CaCl₂ to remove the moisture. Results are displayed in mg/m²/day. The heavy metals content are determined by atomic absorption spectrometer (AAS).

**Deposited dust calculation (aerosediment)**

The quantity of deposited dust calculates by formula:

\[ \text{AS} = \frac{M}{A \cdot t} \text{[mg/m}^2\text{/day]} \]

where are:
- \( m_1 \) - initial weight of dry filter (mg)
- \( m_2 \) - final weight of dry filter plus weight of dust (mg)
- \( M = m_2 - m_1 \) - weight of dust (mg)
- \( A \) – area of collecting vessel (m²)
- \( t \) – time period for sample collection (day)

**Results**

**Measurements for deposited dust and heavy metals in dust**

According to monitoring plan for environment in smelter of Ferronikeli, department of environment perform the measurement of deposited dust (aerosediment) in some monitoring points. The aerosediment measurements are monthly. Standard for aerosediment (according to WHO) is 300 mg/m²/day.

During the year 2008, the measurements of aerosediment are done in 9 points (6 points inside the smelter and 3 outside – urban area). These monitoring places are shown in map below in figure 1, and the short description of their location is explained as follow:
1. In North side of rotary kilns chimney (about 120 meters far from it), close to main electric station.
2. In West side of rotary kilns chimney (distance 300 meter), near by fence.
3. In South-West of plant, near by fence in corner - about 400 meters distance from RK chimney.
4. In South side - near by wastewater treatment plant.
5. In North-East side, near by storage area.
6. In the entrance of plant (main gate)
7. Private house – South-West side of plant, distance about 1 km.
8. Private house – in South-West side of plant, distance about 1.5 km.
9. Reservoirs for water (in North side of plant).

![Figure 1: Monitoring locations for deposited dust during 2008](image)

The measurements were done from January until December 2008. The yearly average values of these measurements of deposited dust and heavy metals in dust are shown in table 1. While, in figure 2 are shown values in graphic form for deposited dust (aerosediment).

**Table 1:** The values of deposited dust and heavy metals

<table>
<thead>
<tr>
<th>No.</th>
<th>Aerosediment (mg/m²/day)</th>
<th>Fe</th>
<th>Ni</th>
<th>Co</th>
<th>Cr</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>334.74*</td>
<td>0.042</td>
<td>0.015</td>
<td>0.016</td>
<td>0.021</td>
</tr>
<tr>
<td>2</td>
<td>219.56</td>
<td>0.031</td>
<td>0.014</td>
<td>0.017</td>
<td>0.022</td>
</tr>
<tr>
<td>3</td>
<td>379.63*</td>
<td>0.066</td>
<td>0.022</td>
<td>0.017</td>
<td>0.022</td>
</tr>
<tr>
<td>4</td>
<td>183.19</td>
<td>0.032</td>
<td>0.023</td>
<td>0.017</td>
<td>0.022</td>
</tr>
<tr>
<td>5</td>
<td>312.04*</td>
<td>0.039</td>
<td>0.007</td>
<td>0.015</td>
<td>0.023</td>
</tr>
<tr>
<td>6</td>
<td>132.53</td>
<td>0.038</td>
<td>0.023</td>
<td>0.016</td>
<td>0.022</td>
</tr>
<tr>
<td>7</td>
<td>112.10</td>
<td>0.026</td>
<td>0.010</td>
<td>0.012</td>
<td>0.017</td>
</tr>
<tr>
<td>8</td>
<td>77.05</td>
<td>0.020</td>
<td>0.011</td>
<td>0.009</td>
<td>0.017</td>
</tr>
<tr>
<td>9</td>
<td>80.81</td>
<td>0.020</td>
<td>0.009</td>
<td>0.008</td>
<td>0.017</td>
</tr>
</tbody>
</table>

*Values above WHO standard
The quality analyze of deposited dust with WDXRF (Wavelength dispersive X-Ray Fluorescence Spectrometry)

The qualities analyze of x-ray specters, generally, not presenting any specific difficulties. Every element which is present in sample appears with some spectral lines. If spectrometer have high resolution, with few exception (spectral interferences) is possible identification of elements that are presents in sample. If the spectral interferences appear, in principle exist possibility to take in consideration other spectral lines of the elements that shown interferences.

The chemical-physical sample state (aggregate state and chemical link) has no influence in quality analyze. For routine analyze is enough spectral lines of series K and L. The series K and L of one element is staying according to wave length far way from each other, so not have over-coverage of spectral lines.

In figure 3 is shown specter of quality analyze of deposited dust. Specter background appears therefore of dispersive of so-called “Bremsstrahlung” at sample surface. Based on spectrum by XRF are found the elements like Fe, Ni, Zn, Ti, Mn, Co, Pd.

Figure 2: Deposited dust for monitoring locations (2008)

Figure 3: The quality analyze of deposited dust – by XRF spectrometer
Conclusion

The values of the deposition of atmospheric dust reported as total solid matter and as dissoluble solid matter, usually used first term. Main disadvantage of collecting container for dust is sticking of solid particles with each-other, so not to allow their dimensions measurement.

In general, from results shown in table 1 and graphically in figure 2 for deposited dust during time period January to December 2008, easy noticed that in 3 points from total 9 measurement points no exceed of WHO standard for deposited dust, but this exceeding are not so high compare with this standard, because these points are in an industrial area, so within plant area. As well as, and heavy metals in deposited dust are not shown any high risk so theirs concentration in dust is low.

From presented results of aerosediments (deposited dust) noticed that no any major problems, and this signify that the electrostatic precipitators work conditions are relatively good, but need to have adequate technical maintenance that the filtering efficiency to be in satisfy level.

References


Lost metals Through Processing Polyminal Lead Zinc in the Flotation Badovc, Kosovo

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Abstract: Metal lost was presented through mineral processing poly-mineral lead-zinc in concentrator Badovc in Kizhnica-Kosova in this study. Reasonable study, this live issue is because in practical processing mineral we have lost metal in flow of Artana. Lost research in metals has an important theoretical, but more practical where we need this mines lead zinc with flotation five year ago restarting production processing. In this base reaches in conclusion for optimal choose processing for decrease louts metal along processing mineral.

Keywords: processing, flotation, feasibility, lost metals, ore deposit, Kosovo

Introduction

Kosova is known with self potential mineralization. Enough with interesting is occurrences and polyminal deposits Pb-Zn-Ag in the S and SE part Trepça Mineral Belt (Hyseni & Large 2003; Hyseni et al., 2010), locate ore fields mineralization more important these: Trepça, Hajvali-Badovc-Kizhnica, Artana, Cornaca etc. (Figure1). Currently according data geological for this mineral belt as presence of lot mineralized occurrence suggests for mineralization potential that can be used with economical interest, not only for today but for future of Pb-Zn-Ag mineralization (Hyseni et al., 2007).

Ores deposition lead and zinc

Mineral deposit lead-zinc “Përroi i ngjyrosur” pertain Artana ore field. Litological and structural factory has indicated setting in space mineralization lead-zinc-siderit-smitsonith and halloysit (Hyseni, Alliu 1999). Ore body has forming metasomathic way in limestone-marble. Foot wall build gneiss, amphibolites schist and phyllite in haning wall. Ore body’s elonged NNW-SSE with dip 60-80° from the west. In deposit Artana mine, we individualize three ore deposits:

Compact ore sulphide weak oxidation and meeting under old mining works.

Compact ore oxidation in pillar old mining middle Century and Ore pyrite.

Mineralogical deposit colors stream (Artana)

According association mineral and combination physical-chemical classification four stage mineralization in mineral deposit. Mineralogical deposit Pb-Zn contents these mineral: FeS₂, ZnS, PbS, FeAsS₂, FeS₂ (marcasite), FeS₁₋ₓ, CuFeS₂, 2PbS Cu₂S Sb₂S₃, 5PbS Sb₂S₃, 4PbS FeS 3 Sb₂S₃, CuAsS₃, CuFeS₃, 4(Fe, Cu) S·(Mg, Al) (OH)₂, Cu₂FeSnS₄, Cu₅FeS₄, Cu₂S, and CuS. Accessory mineral these: cerusite, anglesite, malachite, melanterite, gypsum, limonite, kaolin, halloysite, and waste mineral quartz, calcite, ankerite, and oligonite (Smejkal 1960). Ore structure is coarse compact without deformation tectonic. Inclusion of pyrite in sphalerite, sphalerite in galena is often probably 0.2mm don’t indicate technological processing. Copper sulphate and iron indicate in flotation condition ore in Artana. Mineral deposit according data classifications rich ore Pb (sulk)- 3.79%, Pb (oxide)-0.65%, Zn-5.62%, Ag-143gr/t and FeS₂-57.72% poor ore (pyrite)with Pb (oxide)-0.82%, Zn from 0.10--.38%, Ag-66gr/t and FeS₂-57.52%. From data production we know exploitation simple rich ore due to technological process processing. Oxidation ore lead is above part deposit content 30-35%, when in dip decrease 6-7% and for this we have low step processing recovery.

Technological processing and technological problems

Concentration in Badovic content is two identical sections. Ore from mine bring to feedredoubt capacity 200 t, after goes to feed plate and primary crushing. Through electromagnetic track goes to
grid vibration (50x50mm), reentrant accessory crushing where crushing ore comes into dimension ± 30mm, through connection track (T2), passes three redoubt with capacity 700 t (Figure 2).

Below redoubt is pipe for emptying of ore and electromagnetic vibrations with track (T4) run mill with rods. Mill rods (Φ=80-90mm), finishes here the crushing process. Ore grains with size 74 µ (micron), or 200 mesh floater in surface of the water and go to destine agitator Pb where the flotation process starts, mineral lead give up reagent dose in determined amount (CaO-5000g/t, Dawfroth-100g/t, KBX-200g/t, CuSO4-450g/t, ZnSO4-120g/t, NaCN-0.85g/t) and medium pH=8-8.5. Pulp from agitator lead input eight machine bases and eight machines controllable, reclining lead in six machines and four last reclining where concentrate through track goes into setting lead.

**Table 1.** Statistical data in the enrichment concentrator, Badove

<table>
<thead>
<tr>
<th>Production enrichment</th>
<th>March year 2010</th>
<th>April year 2010</th>
<th>May year 2010</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>shift</td>
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<td>Zn %</td>
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<td>I</td>
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<tr>
<td></td>
<td>II</td>
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<td></td>
<td>III</td>
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<td>4.76</td>
</tr>
<tr>
<td></td>
<td>I</td>
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</tr>
<tr>
<td></td>
<td>II</td>
<td>62.95</td>
<td>4.03</td>
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<tr>
<td>Concentrate Pb</td>
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<td>4.35</td>
</tr>
<tr>
<td></td>
<td>I</td>
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<td></td>
<td>II</td>
<td>1.56</td>
<td>4.23</td>
</tr>
<tr>
<td>Flowing of flotation Pb</td>
<td>III</td>
<td>2.46</td>
<td>5.26</td>
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<tr>
<td></td>
<td>I</td>
<td>4.15</td>
<td>49.32</td>
</tr>
<tr>
<td></td>
<td>II</td>
<td>4.36</td>
<td>49.20</td>
</tr>
<tr>
<td>Concentrate Zn</td>
<td>III</td>
<td>7.81</td>
<td>45.15</td>
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<td></td>
<td>I</td>
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<tr>
<td></td>
<td>II</td>
<td>1.42</td>
<td>1.97</td>
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<tr>
<td>Flowing of flotation Zn</td>
<td>III</td>
<td>1.76</td>
<td>1.81</td>
</tr>
</tbody>
</table>
Figure 2. Enrichment schema ores at Badovec flotation
Lead flowing is entry of zinc where the same way starts the processing of zinc process with same condition as lead, but ones of change value pH from 8.5 to 12 and removes the NaCN as depremination of zinc and adds CuSO₄ as activator of zinc. Flowing of zinc is entry of pyrite and instead KAX of we give NaIPX as collector and H₂SO₄ which makes environment decrease pH. During ore processing in first stage (ores from mine Hajvalia, Badovc and Kizhnica), we didn’t have problems in processing and ore processing was

Figure 3 Presentation of lead concentrates from Artana mine

Ore from Artana mine presented a problem in technological process and we use all technical parameter and special dose reagents. According to this we have collective ore processing instead of lead processing we have zinc processing and vice versa. Therefore according to geological data we think that the main is oxidation of ore and this is reason of this study. We expect that often the reactivation of the mines this year, we think to try the replacement of processing minerals, first flotation zinc, lead and pyrite and to analyze feasibility or amount of zinc in concentrate at Pb and lead in concentrate of zinc then we can come at conclusion regarding feasibility technological process only for Artana ores (stagger). In much case throughout processing at practical (Popovic1979, Hyseni & Durmishaja, 2005) where in place of lead we have more zinc and used a lot of NaCN amount as depremination zinc, which impact at amount and quality of silver (according geological data value of Ag is 27.21 g/t at 1% in Pb this is result analyses BRGM; Anonym, 2001). These data check is tab.1 (Figures 3 & 4), at chemical analyses from year 2010 where amount of zinc concentrate comes in lead concentrate and lead in zinc concentrate (Table1). According by the statistically data from enrichment process (tab.1), we presented (Figures 5 & 6) 3D diagrams of lead and zinc.

Figure 4 Presentation of zinc concentrate from Artana mine
Conclusions

According to result acquired at processing mineral we have low step recovery metals lead and zinc. We need to say that flowing is very high and quality of concentrate is low, whereas consumes of reagent making according standards. Wherefore we propose to change order of flotation, first zinc flotation, lead and pyrite and to analyze feasibility or amount of zinc lead concentrate and lead in concentrate zinc then we can come in conclusion in regarding feasibility technological process. We propose to analyze negotiability theoretical and practical for processing of complex minerals as case Pb-Zn-FeS₂. These problems ask solution to make recovery metals and concentrate but at the same time save electrical energy and standard material \textit{etc}. 
References


Metal Concentration in Artana Ore Flotation Products

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Abstract. In this scientific work, it has been discussed the problem of distribution of elements like Cu, Cd, Bi, Ag and Au during the ore flotation process from Artana mine in the flotation “KIZHNICA” in Kizhnica. Samples have been taken for ten days in row (15-24/10/2009) starting from the entering ore (after the mill with balls), Pb concentrate, Zn concentrate, and waste material. After physical preparation of samples, their chemical analyzing is done with the complexometric method, polarographic, AAS and gravimetric method. It is done also the balancing of metals (Pb, Zn, Cu, Cd, Bi, Ag and Au), and from the obtained results which are shown in the tables 1,2,3 and 4 it is seen the concentration of elements in analyzed materials, distribution, their participation and balance. Meanwhile in the table is seen also their recovery, which is not considered as satisfactory and their losses are relatively high in waste. Therefore, there must be undertaken further research for improvement of their exploitation by applying changes in the quantity of flotation reagents and on milling the lead-zinc ore, and possibly computerizing the process.

Keywords: ore, concentrate, waste, analysis, distribution, losses.

Introduction

Metal gaining in pure condition is mainly carried from their minerals which are found as mixed in the so called ore. As per mineral domination in that way is named the ore too: lead ore, copper ore, zinc ore etc. Therefore these minerals must be concentrated as much as possible in order to be released from other minerals which would make more difficult the process of gaining the base metal (being pyro-metallurgic or hydro-metallurgic).

Mineral concentration in materials that are called concentrates is done in different manners, depending on their physical-chemical features: magnetic, with flotation etc. One of the main ways to make enrichment of Pb-Zn mineral is the process of flotation.

In concentrates, apart from PbS and ZnS minerals which are the dominating ones, there are present also minerals of Cu, Cd, Ag, Bi in sulfite form. As Kosovo is quite wealthy with these minerals (PbS and ZnS), whereas other minerals as their accompanying ones, and now Kosova is only obtaining their concentrates (Pb concentrate and Zn concentrate) which are wanted in market, however, presence of some other minerals are not desired or some others which are desired and based on their concentration in concentrate of lead and zinc concentrate they either get valorized or penalized.

For instance the zinc concentrate which contains Cd is valorized, whereas if it has Bi it is penalized, lead concentrate which contains Ag-and Au it is valorized, whereas in others it is penalized, etc. Therefore we have undertaken researches on distribution (and on participation) of Cu, Cd, Bi, Ag and Au in the products of production process of flotation in Kizhnica, of Pb-Zn ore, of the Artana mine, which is a part of “Trepa”’ mining, metallurgical and chemical complex. Researches are carried for 10 days in continuation (from 15 to 24/10/2009), starting from the entering ore (after milling in the mill with balls), lead concentrate, zinc concentrate and waste (is not gained pyrite and pyrotine). Sample analysis of abovementioned elements is carried with the complex metric method, polarographic method, AAS and gravimetric method. Production capacity (flotation) is 40 t/h. Flotation process is continual for as long as there is ore in the receiving silos.

Materials and Method

Samples have been taken every 15 minutes (in automatic manner) starting from entering ore (after milling the ore in the mill with balls), then lead concentrate and zinc concentrate and the waste.

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All samples are taken in pulp form, and within one shift there are taken about 30 liters. Then samples in the laboratory are filtered under pressure and the solid mass is dried in temperature of 110 °C. Dried samples are homogenized, cut and ground up to 200 mesh (Glotko, Geinrihs, 1969).

Analyzing the elements in the prepared samples is done with these methods: in the entering ore, lead and zinc with the polarographic method, in the base electrolyte of 1 mol/l of amon-acetate, pH = 4.7, copper and cadmium with the polarographic method, in base electrolyte of 1 mol/l amon-hydroxide + 1 mol/l amon-chloride (Visoka, 1980).

In the lead concentrate, lead is determined with complex-metric method, as zinc in zinc concentrate, whereas copper, cadmium and lead in the zinc concentrate and zinc in lead concentrate with polarographic method (Jurist, Korotkova, 1962).

In waste samples, lead, zinc, copper and cadmium are determined with the polarographic method, whereas bismuth in all samples is determined with the AAS method, silver and Gold in all samples is determined with gravimetric method (Sabioncelo, 1965, Rekalic, 1975).

Apart from taking samples it is evidenced the mass of entering ore (t/h), of lead concentrate, of zinc concentrate and waste (t/h), with the aim of balancing the materials and metals.

Obtained results in (%) of metals (Pb, Zn, Cu, Cd, Bi and g/t of Ag and Au) in analyzed samples are given in the table number 1 (for 10 days). In table number 2 is displayed the obtained mass of Pb concentrate, Zn concentrate and waste (t/h), (calculated also in %). In table number 3 are displayed concentrations in (%) average of elements, and their participation in (% of t/h) in analyzed materials.

Results and Conclusion

In the taken samples from the flotation products, except that there are analyzed elements: copper, cadmium, bismuth, silver and gold, are analyzed in lead and zinc as main bearers of the present elements in ore.

Based on gained results, we can see that the main bearer of bismuth, silver and gold is lead, respectively the mineral called galenite (PbS), whereas bearer of cadmium and copper is zinc, respectively mineral of sfalerit (ZnS), and depend on the respective concentrations. Taking into consideration that gained concentrates are not in a high level of enrichment, it has impacted that also conductive elements (Cu, Cd, Bi, Ag and Au) are distributed in the products of flotation—in different concentrations.

These distributions with a good participation rate, are considered as temporary loss, except that in waste are considered as permanent loss. Temporary losses for copper are 13.23% (in lead concentrate), whereas permanent losses are 49.41% (in waste). Temporary losses for cadmium are 6.66% (Pb-concentrate) and permanent losses 39.42% (in waste). Bismuth temporarily is lost in Zn concentrate with 3.71%, whereas permanent loss is 40.0% in waste material. Silver in Zn concentrate goes with mass of 5.56%, whereas in waste goes with mass of 24.60% permanent loss. Because of the level of sensitivity of the used analytical method we could not make final balancing of gold, in order to reflect the distribution and eventual losses. But based on gained results, we can see that gold is accompanier of lead.

Based on the obtained results of samples (entering ore, Pb concentrate, Zn concentrate and the waste) we can conclude that concentration of base elements (Pb and Zn) in ore is different and their concentration in respective concentrates is not satisfactory, and recovery is only 80.17% for Pb and 55.26% for Zn. Also other elements in a high level are spread in products and this is not appropriate, especially we have high losses in waste—irreversible loss.

Therefore, we must spend efforts first of all to have the entering ore with a constant quality (Pb, Zn), and to undertake measures for improvement of technological parameters and to see the possibility of ore milling in better flotation conditions. Especially is important to spend efforts on computerizing the technological process and except obtaining the Pb concentrate and Zn concentrate to obtain the pyrite and pyrotine.
Table 1. Concentration of Pb, Zn, Cu, Cd, Bi, Ag and Au in analyzed samples

<table>
<thead>
<tr>
<th>Date</th>
<th>Sample</th>
<th>Pb</th>
<th>Zn</th>
<th>Cu</th>
<th>Cd</th>
<th>Bi</th>
<th>Ag</th>
<th>Au</th>
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</thead>
<tbody>
<tr>
<td>15.10.2009</td>
<td>Ore</td>
<td>2.00</td>
<td>8.26</td>
<td>0.06</td>
<td>0.02</td>
<td>0.005</td>
<td>88</td>
<td>&lt;0.5</td>
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<tr>
<td></td>
<td>Pb</td>
<td>46.55</td>
<td>3.97</td>
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<td>0.024</td>
<td>1710</td>
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<tr>
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<td>Zn c</td>
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<td>49.88</td>
<td>0.37</td>
<td>0.35</td>
<td>0.003</td>
<td>193</td>
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</tr>
<tr>
<td></td>
<td>Waste</td>
<td>0.49</td>
<td>2.56</td>
<td>0.04</td>
<td>0.01</td>
<td>0.004</td>
<td>32</td>
<td>&lt;0.5</td>
</tr>
<tr>
<td>16.10.2009</td>
<td>Ore</td>
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<td>6.82</td>
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<td>118</td>
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<tr>
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<td>Pb</td>
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<td>0.003</td>
<td>235</td>
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<td>0.03</td>
<td>0.01</td>
<td>0.003</td>
<td>43</td>
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<td>17.10.2009</td>
<td>Ore</td>
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<td>7.35</td>
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<td>0.02</td>
<td>0.007</td>
<td>120</td>
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<tr>
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<td>Pb</td>
<td>54.85</td>
<td>4.20</td>
<td>0.17</td>
<td>0.03</td>
<td>0.059</td>
<td>2014</td>
<td>2.15</td>
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<tr>
<td></td>
<td>Zn c</td>
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<td>42.02</td>
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<td>0.027</td>
<td>1766</td>
<td>1.90</td>
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<tr>
<td></td>
<td>Zn c</td>
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<td>0.003</td>
<td>37</td>
<td>&lt;0.5</td>
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Table 2. Balance of material in the flotation process

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<th>Cu</th>
<th>Cd</th>
<th>Bi</th>
<th>Ag</th>
<th>Au</th>
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<td>5.5</td>
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<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Pb</td>
<td>2.08</td>
<td>5.2</td>
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<td></td>
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<tr>
<td></td>
<td>Waste</td>
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</table>

Table 3. Concentration of metals in flotation products, in %

<table>
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<tr>
<th>Material</th>
<th>Pb</th>
<th>Zn</th>
<th>Cu</th>
<th>Cd</th>
<th>Bi</th>
<th>Ag</th>
<th>Au</th>
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<tbody>
<tr>
<td>Ore</td>
<td>3.43</td>
<td>1.372</td>
<td>4.57</td>
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<td>0.026</td>
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<td>Pb c</td>
<td>2.20</td>
<td>50.00</td>
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<td>Zn c</td>
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<td>2.73</td>
<td>0.056</td>
<td>46.47</td>
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<td>0.361</td>
<td>0.008</td>
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<td>Waste</td>
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<td>1.86</td>
<td>0.664</td>
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Table 4. Balance, recovery and losses of metals

<table>
<thead>
<tr>
<th>Materials</th>
<th>Cu  t/h</th>
<th>Cu  p.m.%</th>
<th>Cd  t/h</th>
<th>Cd  p.m.%</th>
<th>Bi  t/h</th>
<th>Bi  p.m.%</th>
<th>Ag  t/h</th>
<th>Ag  p.m.%</th>
<th>Au  t/h</th>
<th>Au  p.m.%</th>
<th>Recovery</th>
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<td>Ore</td>
<td>40.0</td>
<td>100</td>
<td>0.0257</td>
<td>100</td>
<td>0.0104</td>
<td>100</td>
<td>0.0028</td>
<td>100</td>
<td>5804</td>
<td>100</td>
<td>Pb = 80.17%</td>
</tr>
<tr>
<td>Pb c</td>
<td>2.20</td>
<td>5.50</td>
<td>0.0034</td>
<td>13.23</td>
<td>0.0007</td>
<td>6.66</td>
<td>0.0014</td>
<td>51.07</td>
<td>4048</td>
<td>69.75</td>
<td><strong>1.968</strong></td>
</tr>
<tr>
<td>Zn c</td>
<td>2.08</td>
<td>5.20</td>
<td>0.0075</td>
<td>29.13</td>
<td>0.0060</td>
<td>56.35</td>
<td>0.0001</td>
<td>3.71</td>
<td>322.6</td>
<td>5.56</td>
<td></td>
</tr>
<tr>
<td>Waste</td>
<td>35.70</td>
<td>89.45</td>
<td>0.0127</td>
<td>49.41</td>
<td>0.0042</td>
<td>39.42</td>
<td>0.0011</td>
<td>40.00</td>
<td>1428</td>
<td>24.60</td>
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<tr>
<td>Difference</td>
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<td>+0.15</td>
<td>-0.002</td>
<td>0.15</td>
<td>-0.023</td>
<td>0.0005</td>
<td>+2.43</td>
<td>-0.0002</td>
<td>-5.28</td>
<td>-5.04</td>
<td>-0.09</td>
</tr>
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</table>

References

The Decommissioning of Trino Nuclear Power Plant: Environmental Radiological Impact of Liquid and Gaseous effluents

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Abstract: Radiological effects to the environment around Trino Nuclear Power Plant (Trino NPP) are analyzed. The impact of decommissioning activities is considered using both environmental radiological monitoring data and doses estimated by mathematical models. The environmental monitoring shows no increase of radiological level near the plant. The effects of radioactive effluents coming from the plant can be included in the statistical fluctuation of natural background dose rate. Estimated annual effective dose for the public is less than the 1% of the annual public dose limit recommended by the ICRP. Effluents are discharged from a 100 m high chimney, with continuous monitoring of radioactivity. Liquid effluents are discharged in batch mode and radioactivity concentrations are measured for each discharge. Decommissioning strategy may bring 2 μSv/y due to gaseous release and 8 μSv/y due to liquid to the critical group. The environmental effects due to the decommissioning of the NPP are found insignificant.

Keywords: Radiological Impact, Radioactive Effluents, Decommissioning, PWR.

Introduction

Trino Vercellese Nuclear Power Plant “E. Fermi” (Trino NPP), a 272 MWe Westinghouse Pressurized Water Reactor, has been in operation from January 1, 1965 till March 1985. Trino NPP decommissioning is in the first, preparatory phase, and will end in 2013 (Sogin, 2001). Some of the main preparatory activities to decommissioning have been concluded: Steam Generators (SG) decontamination, modification to water supply system, demolition of some conventional buildings, coating removal in Reactor Building, modifications to electric medium voltage system, modifications to Reactor Building ventilation system. Before decommissioning activities can start, approval must be given by probate authority.

The site is in Piedmont Region, in the west of Padan Plain, traversed by the river Po. To the north, the territory is quite level, rice belt, while to the south Monferrato hills, up to 400 m a.s.l, show primarily grape growing. The site is embedded in a hydrographic grid both natural and artificial. Natural waterways are: Po River, effluents of Sesia River, Dora Baltea River. Artificial ditches are the so called ‘Canali Demaniali Cavour’ used for irrigation purposes. Considering a 10 km radius area around the site, we can count 19 municipalities; the biggest (Trino) has 7600 inhabitants (Istat, 2001). Population in this area is 24385 units, and the medium density is 69 inhabitants / km².

Decommissioning activities radiological impact on population and environment is due both to liquid and gaseous effluents. In the absence of activities, effluents are small (Figure 1), as well as their impacts on the surroundings (Bertani et al., 2007; Arpa, 2006; Arpa, 2003). Decommissioning requires the handling of radioactive components, their decontamination and transport, and these activities are supposed to cause the amount of cumulative dose reported in Table 1. Spent fuel transport outside the site and temporary disposal management activities are not considered being part of decommissioning activities. In the period 2010-2011 nuclear spent fuel will be moved from the plant in order to be reprocessed. Doses reported in Table 1 for already completed activities, like Steam Generators (SGs) decontamination and coating removal, are the final values for workers. Figure 2, Figure 3, and Figure 4 report the foreseen gaseous and liquid releases as consequence of decommissioning activities (Sogin, 2009).

The Effluent Discharge Authorization for liquid and gas sets the quantity of radioactivity that

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can be released from the site in the form of gaseous and liquid dumping, and the Release Limits and Clearance Limits control the release of solid material. These limits are included in the Environmental Impact Study, congruent with European Law (A. Bond, 2003). Probate authority shall confirm these limits when proceeding with Decommissioning Request approval. In this paper we will give a contribution to the analysis of these limits and of the radiological impact of the acceptable effluent releases. Trino Decommissioning strategy may bring 2 μSv/y due to gaseous release and 8 μSv/y due to liquid to the critical group (Sogin, 2009). Italian Law considers these values radiologically non-significant (D.Lgs. 230).

![Figure 1](image1.jpg)

**Figure 1.** Discharged activity (years 2003-2008) and foreseen activity in effluents (2009-2013).

![Figure 2](image2.jpg)

**Figure 2.** Foreseen gaseous discharges due to dismantling activities.

These values should be considered in light of the values of environmental radioactivity in the area. The Regional Agency for Environmental Protection (Agenzia Regionale per la Protezione Ambientale, ARPA) performs periodic measurements of activity on: air particulate, fall out, soil deposition, surface water, ground water, drinking water, organic and mineral river sediment, soil and grass, measurements on food matrix (milk, vegetables), dose evaluations.
Table 1. Foreseen workers exposure dose and timing of decommissioning activities.

<table>
<thead>
<tr>
<th>Activities</th>
<th>Period</th>
<th>man-hour</th>
<th>Dose [mSv-man]</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Reactor Building</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Steam Generators decontamination (SG)</td>
<td>2004</td>
<td>5900</td>
<td>69</td>
</tr>
<tr>
<td>Coating removal in Reactor and Auxiliary Building (RB, AB)</td>
<td>2003-05</td>
<td>44 270</td>
<td>53</td>
</tr>
<tr>
<td>Primary system dismantling preparing activities</td>
<td>2008-09</td>
<td>67 269</td>
<td>14</td>
</tr>
<tr>
<td>Earthquake-proof structures dismantling</td>
<td>2010-11</td>
<td>6720</td>
<td>12</td>
</tr>
<tr>
<td>Large components dismantling</td>
<td>2010-11</td>
<td>78 097</td>
<td>1765</td>
</tr>
<tr>
<td>Other components dismantling</td>
<td>2010-11</td>
<td>29 913</td>
<td>59</td>
</tr>
<tr>
<td>Internals dismantling</td>
<td>2012</td>
<td>81 796</td>
<td>808</td>
</tr>
<tr>
<td>Reactor Pressure Vessel (RPV) dismantling underwater + Neutron Shield Tank (NST)(^a)</td>
<td>2012-13</td>
<td>31 838</td>
<td>132</td>
</tr>
<tr>
<td>Civil and Metal structures decontamination</td>
<td>2013</td>
<td>32 684</td>
<td>31</td>
</tr>
<tr>
<td>Final monitoring</td>
<td>2013</td>
<td>2480</td>
<td>0</td>
</tr>
<tr>
<td>Waste Management Facility (WMF) treatments</td>
<td>2010-13</td>
<td>48 264</td>
<td>241</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td></td>
<td>429 231</td>
<td>3184</td>
</tr>
<tr>
<td><strong>Auxiliary Building</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Removal of material from Purifier Pool</td>
<td>2009</td>
<td>1400</td>
<td>33</td>
</tr>
<tr>
<td>Removal of material from Spent Fuel Pool</td>
<td>2011-12</td>
<td>3400</td>
<td>17</td>
</tr>
<tr>
<td>Systems and components Dismantling (phase 1)</td>
<td>2012-13</td>
<td>55 459</td>
<td>65</td>
</tr>
<tr>
<td>Systems and components Dismantling (phase 2)</td>
<td>2012-13</td>
<td>57 833</td>
<td>173</td>
</tr>
<tr>
<td>Civil and Metal structures decontamination</td>
<td>2013</td>
<td>3000</td>
<td>1</td>
</tr>
<tr>
<td>Final monitoring</td>
<td>2013</td>
<td>2480</td>
<td>0</td>
</tr>
<tr>
<td>Waste Management Facility (WMF) treatments</td>
<td>2010-13</td>
<td>66 936</td>
<td>335</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td></td>
<td>190 508</td>
<td>624</td>
</tr>
<tr>
<td><strong>Waste moving and treatment</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Previous waste treatment</td>
<td></td>
<td>12 440</td>
<td>105</td>
</tr>
<tr>
<td>Resins extraction and treatment (WOX)(^b)</td>
<td>2011-12</td>
<td>12 440</td>
<td>105</td>
</tr>
<tr>
<td><strong>Solid Waste moving and treatment</strong></td>
<td></td>
<td>7180</td>
<td>40</td>
</tr>
<tr>
<td>Compaction 220 l drums</td>
<td>2012-13</td>
<td>4680</td>
<td>25</td>
</tr>
<tr>
<td>Handling of drums</td>
<td>2009-13</td>
<td>2500</td>
<td>15</td>
</tr>
<tr>
<td>Waste transfer to national repository</td>
<td></td>
<td>24 812</td>
<td>72</td>
</tr>
<tr>
<td>Waste container cat. I(^c)</td>
<td>2020-22</td>
<td>15 100</td>
<td>31</td>
</tr>
<tr>
<td>Waste container cat. II</td>
<td>2020-22</td>
<td>9528</td>
<td>40</td>
</tr>
<tr>
<td>Waste container cat. III</td>
<td>2020-22</td>
<td>184</td>
<td>1</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td></td>
<td>44 432</td>
<td>217</td>
</tr>
<tr>
<td><strong>Repositories decontamination</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Temporary repositories decontamination</td>
<td>2023-24</td>
<td>3000</td>
<td>1</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td></td>
<td>3000</td>
<td>1</td>
</tr>
<tr>
<td><strong>Final total</strong></td>
<td></td>
<td>667 171</td>
<td>4026</td>
</tr>
</tbody>
</table>

\(^a\) the Neutron Shield tank is an annular tank with a wall thickness of 16 mm, and 76 cm water depth, surrounding the vessel. Now, the tank is filled with water with addition of potassium chromate to control corrosion. It will be unloaded before reactor vessel dismantling start.

\(^b\) wet oxidation process;

\(^c\) waste categories for Italy are reported in ENEA (1987), Guida Tecnica 26.
Performed analyses are mostly gamma spectrometry, $^3$H distillation and liquid scintillation, radiochemical analysis of Plutonium and Strontium, total alpha and beta activity measurement. The most interesting radionuclides for gamma spectrometry analysis on air particulate are $^{60}$Co, $^{137}$Cs and $^{131}$I. Usually, the measures performed on concentration for these radionuclides give the Minimum Detectable Concentration (MDC), and so the value of MDC is considered in ARPA reports. The MDC may vary between $1e-4$ and $4e-5$ Bq/m$^3$ for $^{137}$Cs according to air volume and acquisition time. No artificial radionuclides have been detected in more than insignificant levels. Po River sediments are sampled up stream and down stream the Site. They show levels of artificial radionuclides comparable to other regional values (the maximum value in 2008 was $9.87 \pm 1.70$ Bq/kg), with no observable cumulating situations (ARPA, 2009) and minimal variation between the up stream and down stream samples. Between the monitored radionuclides ($^{241}$Am, $^{60}$Co, $^{134}$Cs, $^{137}$Cs, $^{131}$I) $^{131}$I can be ascribed to hospital activities. The medium dose received by the population of Piedmont Region is 3.827 mSv/y, the 39% of which is due to radon inhalation, the 31% to medical diagnostics, the 28% to natural radionuclides and the remaining percent to artificial radionuclides (Arpa, 2007).

2. Effluents

Figure 2, 3 and 4 show the estimate of liquid and gaseous discharge during decommissioning (Sogin, 2009). Decommissioning plan considers the period from 2007 to 2013 including the main radioactivity discharge, when the main activities in Reactor Building will take place, as can be seen in Table 1. The main part of radioactivity is held inside the Reactor Building and Auxiliary Building, therefore the main part of activity in the discharge comes from activities performed inside these buildings or on materials belonging to them. Effluent analyses are performed periodically, with the characteristics and instrumentations reported in Tables 2 and 3. Four monitoring systems control the discharging effluents (RIC 101, RIC 102, RIC 103, RIC 104 e RE 308), and one controls liquid effluents (RIC 111). All indications, signals, alarms, registrations and regulations of effluents monitoring systems are reported inside the Plant.

2.1. Gaseous effluents

Gaseous effluents are: ventilation air belonging to Reactor Building, Auxiliary Building, Radioactive Waste Facility, Radiation Protection and Radiochemistry Laboratories, Controlled Area. Before being released to the environment, air is filtered by HEPA filters and it is monitored. Cutting activities are of major concern, because of the production of contaminated dusts and their spread in the working area (Bonavigo et al., 2009; DOE, 1994). During dismantling activities filtering devices (extractor fan, cabins or other) will be placed near the cutting zone, in order to catch, convey, and filter fumes and dust produced by the cutting tool, reducing the amount of radioactivity that will be discharged to the environment. All effluents belonging to the containment flow to the chimney, 100 m high.
Figure 4. Discharged activity in liquid and gas effluents (2002-2008) and foreseen activity (2009-2013) in relation with Reactor Building decommissioning activities.
### Table 2. Characteristics of activity monitors for discharges control.

<table>
<thead>
<tr>
<th>Monitor</th>
<th>Use</th>
<th>MDC</th>
<th>Calibration</th>
<th>Periodical check</th>
</tr>
</thead>
<tbody>
<tr>
<td>RIC 101</td>
<td>Monitor activity of particulate in the atmosphere of the containment</td>
<td>0.03 Bq/m³ (α) 0.2 Bq/m³ (β)</td>
<td>Biennial calibration with ⁶⁰Co, ¹³⁷Cs solid state</td>
<td>Monthly operational checks of instrument performance</td>
</tr>
<tr>
<td>RIC 102</td>
<td>Monitor activity of particulate in the atmosphere discharged from the chimney</td>
<td>0.03 Bq/m³ (α) 0.19 Bq/m³ (β)</td>
<td>Biennial calibration with ⁹⁵Am, ⁹⁰Sr</td>
<td>Twice-monthly operational checks of instrument performance</td>
</tr>
<tr>
<td>RIC 103</td>
<td>Monitor activity of gas in the atmosphere of the containment</td>
<td>0.93 Bq/m³ (β)</td>
<td>Biennial calibration with ⁸⁵Kr</td>
<td>Monthly operational checks of instrument performance with ³⁶Cl</td>
</tr>
<tr>
<td>RIC 104</td>
<td>Monitor activity of gas in the atmosphere discharged from the chimney</td>
<td>0.93 Bq/m³ (β)</td>
<td>Biennial calibration with ⁸⁵Kr</td>
<td>Monthly operational checks of instrument performance ³⁶Cl</td>
</tr>
<tr>
<td>RIC 111</td>
<td>Monitor activity of liquid effluents discharged into the river</td>
<td>5.9 Bq/l</td>
<td>Biennial calibration (γ) with standard QCY 48 source a</td>
<td>Monthly operational checks of instrument performance</td>
</tr>
</tbody>
</table>

*a Composition of QCY 48 source: ²⁴ⁱAm, ⁸⁹Cd, ⁶⁸Co, ⁶⁸⁰Ce, ²⁰⁳Hg, ¹¹³Sn, ⁸⁵Sr, ¹³⁷Cs, ⁸⁸Y, ⁶⁰Co.*

### Table 3. Characteristics of activity measurements.

<table>
<thead>
<tr>
<th>Measurement</th>
<th>Sample</th>
<th>Frequency</th>
<th>Instrumentation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Determination of total β activity on particulate</td>
<td>RIC 102</td>
<td>Continuous</td>
<td>β activity detector</td>
</tr>
<tr>
<td>Determination of noble gas total β activity</td>
<td>RIC 104</td>
<td>Continuous</td>
<td>β activity detector</td>
</tr>
<tr>
<td>Determination of halogens radioactivity</td>
<td>RE 308</td>
<td>Continuous</td>
<td>γ radiation detector</td>
</tr>
<tr>
<td>Determination of total α activity on particulate</td>
<td>Filter of RIC-102 monitor</td>
<td>Six-monthly</td>
<td>ZnS probe</td>
</tr>
<tr>
<td>Determination of activity on particulate</td>
<td>Filter of RIC-102 monitor</td>
<td>Monthly</td>
<td>γ spectrometry on representative samples</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Annual</td>
<td>α activity detector</td>
</tr>
<tr>
<td>Determination of tritium activity</td>
<td>Sample of ventilation air coming from: Nuclear containment Auxiliary building a Fuel handling area a RWD building a</td>
<td>Monthly</td>
<td>Extractor fan and liquid scintillator</td>
</tr>
<tr>
<td>Determination of ⁹⁰Sr activity on particulate</td>
<td>Filter of RIC-102 monitor</td>
<td>Six-monthly</td>
<td>Liquid scintillator</td>
</tr>
</tbody>
</table>

*The calculation of discharged activity will take into account possible ventilation fan malfunction.*
\[
\sum_{i=1}^{n} \frac{A_i}{L_i} < 1 \quad \text{in one solar year}
\]

Ai is the released activity of i-th radionuclide;

Li is the value of discharged activity of i-th radionuclide that causes 10 μSv/y dose to an individual belonging to the critical group.

\[
\sum_{i=1}^{n} \frac{A_i}{L_i} < 1 \quad \text{in one solar year}
\]

Ai is the released activity of i-th radionuclide,

Li is the value of discharged activity of i-th radionuclide that causes 1 μSv/y dose to an individual belonging to the critical group.

<table>
<thead>
<tr>
<th>Radionuclide</th>
<th>Li (Bq) a</th>
<th>Radionuclide</th>
<th>Li (Bq) a</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{241}$Am</td>
<td>1.626E+08</td>
<td>$^{241}$Am</td>
<td>8.60E+10</td>
</tr>
<tr>
<td>$^{14}$C</td>
<td>2.469E+12</td>
<td>$^{14}$C</td>
<td>5.87E+11</td>
</tr>
<tr>
<td>$^{60}$Co</td>
<td>3.623E+09</td>
<td>$^{60}$Co</td>
<td>1.29E+12</td>
</tr>
<tr>
<td>$^{134}$Cs</td>
<td>3.210E+09</td>
<td>$^{134}$Cs</td>
<td>3.06E+11</td>
</tr>
<tr>
<td>$^{137}$Cs</td>
<td>3.899E+09</td>
<td>$^{137}$Cs</td>
<td>4.44E+11</td>
</tr>
<tr>
<td>$^{135}$Eu</td>
<td>1.307E+10</td>
<td>$^{135}$Eu</td>
<td>2.89E+12</td>
</tr>
<tr>
<td>$^{152}$Eu</td>
<td>9.174E+09</td>
<td>$^{152}$Eu</td>
<td>2.63E+12</td>
</tr>
<tr>
<td>$^{55}$Fe</td>
<td>4.386E+10</td>
<td>$^{55}$Fe</td>
<td>3.39E+13</td>
</tr>
<tr>
<td>$^{3}$H</td>
<td>9.948E+10</td>
<td>$^{3}$H</td>
<td>1.35E+15</td>
</tr>
<tr>
<td>$^{85}$Kr</td>
<td>9.524E+16</td>
<td>$^{54}$Mn</td>
<td>3.64E+16</td>
</tr>
<tr>
<td>$^{54}$Mn</td>
<td>3.521E+10</td>
<td>$^{54}$Ni</td>
<td>5.47E+14</td>
</tr>
<tr>
<td>$^{59}$Ni</td>
<td>3.401E+11</td>
<td>$^{60}$Ni</td>
<td>2.25E+14</td>
</tr>
<tr>
<td>$^{60}$Ni</td>
<td>1.408E+11</td>
<td>$^{239}$Pu</td>
<td>7.13E+10</td>
</tr>
<tr>
<td>$^{239}$Pu</td>
<td>1.342E+08</td>
<td>$^{239}$Pu</td>
<td>3.98E+12</td>
</tr>
<tr>
<td>$^{235}$Pu</td>
<td>7.435E+09</td>
<td>$^{125}$Sb</td>
<td>6.38E+12</td>
</tr>
<tr>
<td>$^{125}$Sb</td>
<td>1.626E+10</td>
<td>$^{90}$Sr</td>
<td>7.92E+11</td>
</tr>
<tr>
<td>$^{90}$Sr</td>
<td>6.410E+08</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

a these values are those of the present Effluent Discharge Authorization, which causes 1 μSv/y dose to an individual belonging to the critical group due to gaseous effluents discharge, and 10 μSv/y due to liquid discharge.

Table 4. Effluent Discharge Formula

This is the only point of gaseous effluent discharge to the environment. Effluent filters are HEPA filtering systems (>99.95% global efficiency for 0.3 micrometers particulate) with pre-filtering (>78% efficiency for 0.5 micrometers particulate). The chimney air flow rate is approximately 110 000 m³/h, and the air flowing from the Reactor Building is 1 Vol/h (approximately 30 000 m³/h).

To make an evaluation of gaseous effluents these isotopes are considered: $^{3}$H, $^{60}$Co, $^{55}$Fe, $^{63}$Ni, $^{137}$Cs and to a small degree $^{65}$Ni, $^{125}$Sb, $^{90}$Sr, $^{134}$Cs, $^{152}$Eu, $^{154}$Eu and alpha emitters. $^{85}$Kr has been neglected because in 2003 the spent fuel has been stored in dry casks, ceasing the release of this gas. $^{133}$Xe, other noble gases and halogens have been neglected because their level is decayed to non-measurable quantities (Sogin, 2009). The estimated total discharge of gaseous effluents is 43 GBq, almost totally composed by $^{3}$H (nearly at 100%).
2.2. Liquid Effluents

Liquid waste are floor drain, demineralization and regeneration liquid waste from plant water purification system, liquid waste becoming from decontamination activities, from radiochemistry laboratory, from decontamination showers and changing rooms, liquid waste produced by cleaning of contaminated clothes. Some of these liquids already undergo evaporation. Analyses results and chemico-physical characteristics of the fluid are determining in the choice of the treatment (filtering, chemical processing on ion exchange resins).

Analyses are performed on samples of the liquid contained in the tanks that will be discharged through the specific system into the Po River. After that, measurements are performed using a specific line with a continuous monitoring system which allows a steady control of the discharging gamma activity. The estimated total production of radioactivity in liquid waste is 59.7 GBq, while the estimated total discharge after treatment is 27.2 GBq, for the main part (67%) due to $^3$H (Sogin, 2009). Specific activity highly depends upon the origin of the waste and the function it had in the system. Representative radionuclides are: $^3$H, $^{60}$Co, $^{54}$Mn, $^{110}$Ag, $^{125}$Sb, $^{137}$Cs, $^{134}$Cs, $^{90}$Sr, $^{55}$Fe, $^{60}$Ni, alpha emitters. The treatments for reducing waste activity are not applied uniformly, for example no treatment is applied to laundry waste, decontamination showers and changing rooms wastes because detergents may damage resins. The other waste is treated by the purification system, formed by filtering devices and demineralizers. Activity reduction factors depend on the radionuclide, the kind and the proximity to exhaustion of the purifier. Excluding Tritium that can not be retained, these medium reduction factors are assumed for a mixed bed purifier (activity reduction factors are the ratio between activity before and after treatment): 10 for $^{60}$Co, 3 for $^{137}$Cs and $^{134}$Cs, 10 for $^{90}$Sr, $^{55}$Fe and $^{60}$Ni; 5 for $^{239}$Pu equivalent and total alpha.

3. Emission related dose

Dose calculation can be performed using many different models (IAEA 2005; IAEA, 2000; Kocar 2009). It is usually performed with specific calculation codes which allow the user to easily know the dose received by the critical group, providing all the characteristic emission parameters (kind of discharge, activity, isotopic composition, time of discharge, point of discharge); meteorological conditions, soil conditions and water basin features for transport modeling; all the characteristic receptor parameters (position and distribution of population, food and recreation habits, age distribution and so on).

The emission related dose is calculated using the GENII code, which correlates emission to dose through exposure pathways. The code has been developed by the Pacific Northwest National Laboratory (PNNL, Richland, Washington) for the Environmental Protection Agency (EPA), Office of Radiation and Indoor Air. The dosimetry model the code considers is the ICRP model of publications 26, 30, 48, updated by publications 56 and 72 (Napier, 1990).

The critical group is the most susceptible to damage by a particular form of pollution, usually relatively homogeneous with respect to age, diet, or other life habits, which are relevant to exposure. The critical group has been selected considering population distribution on the territory, food habits, and all those habits that could lead to an effect on exposure, as also the characteristics of the area (prevalent wind direction, for example).

Radiological impact for gaseous effluents has been calculated within a 10 km radius area surrounding the Plant chimney, and with regards to 0 m and 100 m discharge high. The dominant radionuclide is $^3$H, contributing for the 99% to the total dose; critical exposure pathway is inhalation (Sogin, 2009).

Radiological impact for liquid effluents has been calculated on the area located on Po River, for 20 km after discharge point, including the area irrigated by some artificial ditches. The critical radionuclide is $^{137}$Cs. The $^{137}$Cs related dose is the 64% of the total dose for liquid release, and the critical exposure pathway is ingestion (Sogin, 2009).

3.1. Definition of Effluent Discharge Authorization

The maximum quantity of radioactivity that can be released from the site in the form of gaseous and liquid dumping is set by the Effluent Discharge Authorization (IAEA, 2000). It contains different restrictions, in the form of an Effluent Discharge Formula (Table 4), which is radionuclide specific and depending on the kind of discharge (liquid, gas) (Sogin, 2009). Using the Effluent Discharge Formula
we can easily know the dose to the critical group coming from the dump, as result of the simulations performed with GENII, as previously explained.

Effluent Discharge Authorization takes the form of a set of constrains on radionuclides quantity in the discharge, that are measured at its point of release to the environment. These constrains assure that the radiological dose to the critical group due to the discharged mix of effluents will not overcome dose law limits.

Particulate contamination in the air is monitored by filtration (pumping air through filter media and measuring the radioactivity on the filter), with a moving filter paper and by an alpha detector and a beta detector suitably screened. Gas monitoring is accomplished with a screened expansion chamber with a beta detector. Halogens monitoring system is supplied with activated charcoal bed to trap halogens which are measured by a gamma detector. All measurement channels are supplied with internal calibrated sources for periodical check.

Measurement methodology and instrumentation are of primary importance, in particular its reliability and the right operation of the measurement channel, its Sensibility, and Minimum Detectable Activity (MDA) also, in case of analytical analysis. Instrumentation limits involve a certain amount of radioactivity that can be released within the controlled discharged without being rightly revealed by the monitoring system.

The Effluent Discharge Formula proposed by Sogin (Società Gestione Impianti Nucleari, it is the company responsible for the execution of activities related to the dismantling of the dismissed Italian nuclear power plants) may lead to population doses considered by Italian law radiologically non-significant (D. Lgs. 07/05/2001; D. Lgs. n° 230). Effluent Discharge Formula is then set using a backward procedure: constrains are set providing the value of dose which we know would be consequent to that radioactivity discharge. It complies with dose law constraints (1 mSv/y for population). Moreover, the maximum dose to the critical group may be limited to lower values: 8 μSv/y due to liquid discharge and 2 μSv/y due to gaseous discharge in this case.

The discharge of the 100% of the present Effluent Discharge Formula causes 1 μSv/y dose to an individual belonging to the critical group due to gaseous effluents discharge, and 10 μSv/y due to liquid discharge. In Figure 5 the foreseen percent of the Effluent Discharge Formula for the years 2009-2021 is reported.

The maximum Effluent Discharge Authorization commitment, for liquid effluents, for decommissioning activities from 2009 on, is slightly over 1.1%, in 2012 (parallel to the Spent Fuel Pool and Reactor Cavity drain, corresponding to 8.8E-02 µSv/y) (Figure 5; Sogin, 2009).

The maximum Effluent Discharge Authorization commitment for gaseous effluents is less then the 0.011%, in 2011 (parallel to the main contaminated and activated component cutting, corresponding to 2.2E-04 µSv/y) (Figure 5; Sogin, 2009). Effluent Discharge Formula is reported in Table 4. It refers to an annual continuous discharge.

3.2. Definition of the Minimum Detectable Activity

Prior to performing measurements, the detection sensitivity of the equipment proposed for use must be evaluated to ensure that adequate levels can be detected. After a measurement has been made, it is then necessary to determine whether or not the result can be distinguished from the instrument background response of the measurement system. The parameters used are: Critical level Minimum detectable concentration (MDC) and Detection limit. The critical level is the net response level, in counts, at which the detector output can be considered above background. The detection limit is the net response level, in counts, that can be expected to be seen with a detector with a fixed level of certainty. The MDC is the a priori net activity level above the critical level that an instrument can be expected to detect 95% of the time. This value should be used when stating the detection capability of an instrument. For direct measurements, the MDC is the detection limit multiplied by an appropriate conversion factor to give units of activity. Assuming that a system has a background response and that random uncertainties and systematic uncertainties are accounted for separately, these parameters can be calculated using statistics relations (MARSSIM, 2000; NUREG, 1985; ORTEC, 2006).

An approach for including uncertainties into the MDC calculation is recommended, so that the MDC is the a priori net activity level above the critical level that an instrument can be expected to detect 95% of the time (MARSSIM, 2000). For analytic laboratory sample analyses, the MDC is defined as the concentration of an analyte that must be present in a laboratory sample to give a
specified probability of obtaining a measured response greater than its critical value, leading one to conclude correctly that there is analyte in the sample. The calculation of the nominal MDC is complicated by the fact that some input quantities in the mathematical model, such as interferences and the chemical yield, which have a substantial impact on the MDC, may vary significantly from measurement to measurement (MARLAP, 2004).

**Figure 5.** Evaluation of the use of Effluent Discharge Authorization

From a conservative point of view, it is better to overestimate the MDC for a measurement method. The detection sensitivity for a given application can be improved by: selecting an instrument with higher detection efficiency or with lower background, decreasing the scanning speed, or, increasing the measuring time, or when possible, increasing the size of the effective probe area without significantly increasing the background influence. The instrument should be calibrated for the radiations and energies of interest at the site. This calibration should be traceable to an accepted standards organization. Routine operational checks of instrument performance should be performed (MARLAP, 2004).

**Figure 6.** Example of exposure pathway to man in assessing effective dose due to radionuclides discharged from the NPP.
3.3. Radioactivity transfer factor

An example of exposure pathway to man in assessing effective dose due to radionuclides discharged from the NPP is reported in Figure 6. The transfer of radionuclides in the biosphere is a major issue in the calculation of the final dose to man. The moving of radionuclide from an environmental matrix to the following in an exposition pathway is dominated by complex mechanisms of retention and removal, from the transfer factor of the radionuclide (ICRU, 1998).

For example, concentration of radionuclide in leafy vegetable (Bq/Kg) is to be calculated for both pathways of direct deposition onto vegetation and the root uptake of radioisotope deposited into the ground. The parameters used to perform this calculation are: annual average is the deposition velocity of radionuclide, the radiological decay constant, fraction of deposited material retained on vegetation, the effective removal rate, the time that vegetation is exposed to radionuclides during the growing season, the agricultural productivity, the transfer factor of radionuclide from soil to vegetation, the time of long-term accumulation of radioisotope in soil, the density of the soil. Mobility and transfer of radionuclides in the soil-plant system are specific to soil type and land use.

The choice of the value of these parameters is site specific, although many examples can be found in literature. Many variables affect the numerical value of these parameters, and the mechanism of radionuclides transfer itself is not well known (Higley, 2007; IAEA, 2009; IAEA, 2006; IAEA, 1994).

4. Conclusions

Decommissioning activities for Trino Vercellese NPP are in the first, preparatory phase, and will end in 2013. In absence of activities on contaminated or activated material, Trino facility releases trivial quantities of radioactivity in the environment, without radiological significant effects.

Radionuclides emissions, during the whole decommissioning, will not be responsible for significant changes in radionuclides concentrations in environmental matrices concerning the involved area. Regarding population, Sogin outlines a series of liquid and gaseous releases which, due to the definition of the Effluent Discharge Authorization, will cause effects under significance according to Italian law.

Regarding emissions, the dominant radionuclide is 3H, which accounts for the main part of gaseous effluents and a quantity of liquid too. Regarding population dose, the main radionuclide is the 3H again, for gaseous effluents, and 137Cs for liquids. The value of population dose is not significant when compared to medium dose received by the Italian population. The level of decommissioning related doses is guaranteed by the respect of the Effluent Discharge Formula, which ensures that, for provided radioactivity measurements at the point of discharge, law constraints will be fulfilled.

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ICRU International Commission on Radiation Units and Measurements (1998) Quantities, Units and Terms in Radiecology, Bethesda, MD.


Effects of Land Use/Cover Change on the Soil Properties in River Sio Catchment

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Abstract: The diversity of land use/cover change in affecting the quality of physical and chemical properties of soils and reducing vegetation cover is of a growing concern in Uganda today. Specifically, the study intended; to determine the effects of land use/cover change on the soil properties in River Sio catchment. The effects of land use/cover utilization types on soil properties were dependent on conversions of grasslands to the growing of sugarcanes, cassava & maize, perennial to annual crops, soil depth and watershed positions. A composite soil sample was randomly collected from each location along the selected transects totalling to 272 soil samples taken at two soil depths (0-15cm & 15-30cm) for comparisons. The results showed that; the effect of the conversion of grasslands into agricultural fields primarily induced changes in nitrogen for the topsoil (0-15cm) while in nitrogen, organic matter and phosphorous for the subsoil (15-30cm) in both mid and downstream sections of the watershed. Therefore this study information on the physio-chemical soil properties will help natural resource managers and other stakeholders to understand how soil properties are affected under intensive management systems and this will help them to determine better farming practices which can retain soil nutrients to be undertaken by the farmers to reduce on soil degradation.

Key Words: upstream/downstream, soil physio-chemical properties, land use/cover change

Introduction

Land use and land cover conversion can lead to deterioration in the physical and chemical properties of soils (Lal, 1996). This deterioration can also subsequently affect water quality, biodiversity and global climatic systems (Priess et al., 2001). The most dramatic loss of soil organic matter, soil humic substances, biological activity and soil physical quality are undoubtedly associated with land cover removal and subsequent poor soil management techniques (Lal, 1981; Khresat et al., 2008). These practices largely lead to soil degradation which is one of the world’s major socio-economic and environmental problems, affecting one billion people in 110 countries worldwide and is prevalent across about 40 percent of the Earth’s surface (UNEP, 1997). Important to note is that the property of ecosystems that is likely to change with land use/cover changes is carbon (C) sequestration in soil organic matter (Powers, 2004) and this is further accelerated by poor land management practices caused out of ignorance, socio-economic, cultural and political forces (Rusoke et al., 2000). It is estimated that about 320 million ha, or about one quarter of Africa’s dry lands, are affected by different types of soil erosion caused as a result of massive land cover clearance (UNEP, 1997).

These agricultural practices are responsible for soil nutrient mining in East Africa which is among the highest in Sub-Saharan Africa, with an estimated annual nutrient depletion rate of 41kg nitrogen (N), 4kg phosphorus (P) and 31kg potassium (K) per hectare (Bekunda et al., 2002). Presently, the Sio catchment is experiencing massive expansions and intensifications of agricultural activities. These activities have positively or negatively affected the catchment’s soil physio-chemical properties and largely reduced the areas covered by various land use/cover types. Maitima et al., (2004) and Makalle et al., (2008) coincide that the agricultural activities in the Lake Victoria basin have expanded by 70% between 1958 and 2001, leaving only isolated pockets of land cover. Unfortunately, the effects land use/cover change on the soil physio-chemical properties within the catchment have received the least of attention. Therefore the study will generate information which

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will be enable land managers, scientists, and policy makers to make better informed decisions regarding land use/cover utilization and sustainable development.

**Materials and Methods**

*Description of Area of study*

The study was carried out in the trans-boundary River Sio catchment. The River has its source from the footsteps of Mt. Elgon and has a catchment area of about 1,500 km². It originates in Kaujai and Luucho Hills in Bungoma District, Kenya at an altitude of 1800m. The River flows through Bungoma, Teso and Busia Districts into Berkeley Bay and drains into Lake Victoria in Uganda. The catchment forms a significant base for the livelihood of small scale farmers engaged in mixed farming, depending on agriculture, fishing and livestock keeping.

![Study area](image)

**Figure 1.** Study area

*Assessment of the effects of land use/cover change on the soil physio-chemical properties*

A total of 272 locations representing four major agricultural land uses with similar management history namely sugarcanes, maize, cassava and grasslands were randomly selected for soil sampling. All these locations were initially grasslands prior to current land uses. A composite soil sample was collected from each location at two soil depths 0-15 cm and 15-30 cm. The land use/cover types with similar management history and located in the same soil units were compared in terms of soil properties. Properties of soils under three agricultural land use types were then compared with grasslands as a control. The soil composite samples were collected along the selected transects in each village from both the midstream and downstream (downstream transects were - Lukhalare, Namusuba, Nangondo, Bushera, Mororo, Buswahili & Sitengo while in the midstream - Mabunge, Katome, Musokoto, Walatsi, Lelekwe, Nyaranga & Anbangusi). The soil samples were delivered to Makerere University Department of Soil Science Laboratory for physio-chemical Analysis following the Standard Soil Laboratory Analysis procedures as described by Okalebo *et al.*, (2002). The data collected from the soil samples was categorized according to land use/cover for comparisons by an application of two-way ANOVA ($P<.05$) using Genstat Software to separate the means.
Results
The effects of land use/cover change on the soil properties given in Tables 1 and 2.

Table 1. Showing the mean values for selected physio-chemical soil properties in Sio catchment (0-15cm depth)

<table>
<thead>
<tr>
<th>Properties</th>
<th>Depth (cm)</th>
<th>Sugar canes</th>
<th>Cassava</th>
<th>Maize</th>
<th>Grasslands</th>
<th>ANOVA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Clay</td>
<td>0-15</td>
<td>28.9</td>
<td>31.8</td>
<td>23.4</td>
<td>19.5</td>
<td>*</td>
</tr>
<tr>
<td>Sand</td>
<td>0-15</td>
<td>27.7</td>
<td>28.1</td>
<td>21.8</td>
<td>21.1</td>
<td>*</td>
</tr>
<tr>
<td>Silt</td>
<td>0-15</td>
<td>24.9</td>
<td>21.1</td>
<td>24.8</td>
<td>21.7</td>
<td>*</td>
</tr>
<tr>
<td>pH</td>
<td>0-15</td>
<td>5.4</td>
<td>5.4</td>
<td>5.5</td>
<td>5.7</td>
<td>n.s*</td>
</tr>
<tr>
<td>Mid stream</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>OM (%)</td>
<td>0-15</td>
<td>3.3</td>
<td>3.3</td>
<td>4.2</td>
<td>3.3</td>
<td>n.s*</td>
</tr>
<tr>
<td>P (mg/kg)</td>
<td>0-15</td>
<td>2.3</td>
<td>2.8</td>
<td>2.6</td>
<td>2.8</td>
<td>n.s*</td>
</tr>
<tr>
<td>N (%)</td>
<td>0-15</td>
<td>0.2</td>
<td>0.2</td>
<td>0.3</td>
<td>0.2</td>
<td>*</td>
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<tr>
<td>Clay</td>
<td>0-15</td>
<td>34.5</td>
<td>26.2</td>
<td>37.2</td>
<td>30.2</td>
<td>*</td>
</tr>
<tr>
<td>Sand</td>
<td>0-15</td>
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<td>26.6</td>
<td>28.8</td>
<td>23.6</td>
<td>n.s*</td>
</tr>
<tr>
<td>Silt</td>
<td>0-15</td>
<td>26.0</td>
<td>19.2</td>
<td>25.2</td>
<td>13.6</td>
<td>*</td>
</tr>
<tr>
<td>Down stream</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>pH</td>
<td>0-15</td>
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<td>5.8</td>
<td>5.9</td>
<td>5.9</td>
<td>n.s*</td>
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<tr>
<td>OM (%)</td>
<td>0-15</td>
<td>3.4</td>
<td>3.6</td>
<td>4.0</td>
<td>2.5</td>
<td>n.s*</td>
</tr>
<tr>
<td>P (mg/kg)</td>
<td>0-15</td>
<td>4.2</td>
<td>4.2</td>
<td>3.4</td>
<td>4.9</td>
<td>n.s*</td>
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<tr>
<td>N (%)</td>
<td>0-15</td>
<td>0.20</td>
<td>0.19</td>
<td>0.23</td>
<td>0.19</td>
<td>n.s*</td>
</tr>
</tbody>
</table>

*Significant at P<0.05, n.s* Not significant at P<0.05

Table 2. Showing the mean values for selected physio-chemical soil properties in Sio catchment (15-30cm depth)

<table>
<thead>
<tr>
<th>Properties</th>
<th>Depth (cm)</th>
<th>Sugar canes</th>
<th>Cassava</th>
<th>Maize</th>
<th>Grasslands</th>
<th>ANOVA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Clay</td>
<td>15-30</td>
<td>29.1</td>
<td>20.7</td>
<td>28.5</td>
<td>26.6</td>
<td>*</td>
</tr>
<tr>
<td>Sand</td>
<td>15-30</td>
<td>29.5</td>
<td>21.3</td>
<td>21.1</td>
<td>21.8</td>
<td>*</td>
</tr>
<tr>
<td>Silt</td>
<td>15-30</td>
<td>24.0</td>
<td>19.8</td>
<td>23.5</td>
<td>21.1</td>
<td>n.s*</td>
</tr>
<tr>
<td>pH</td>
<td>15-30</td>
<td>5.7</td>
<td>5.5</td>
<td>5.5</td>
<td>5.6</td>
<td>n.s*</td>
</tr>
<tr>
<td>Mid stream</td>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>OM (%)</td>
<td>15-30</td>
<td>2.8</td>
<td>2.6</td>
<td>3.1</td>
<td>3.0</td>
<td>*</td>
</tr>
<tr>
<td>P (mg/kg)</td>
<td>15-30</td>
<td>2.9</td>
<td>2.2</td>
<td>2.6</td>
<td>2.5</td>
<td>n.s*</td>
</tr>
<tr>
<td>N (%)</td>
<td>15-30</td>
<td>0.18</td>
<td>0.17</td>
<td>0.21</td>
<td>0.19</td>
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<tr>
<td>Clay</td>
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</tr>
<tr>
<td>Sand</td>
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<td>n.s*</td>
</tr>
<tr>
<td>Silt</td>
<td>15-30</td>
<td>26.5</td>
<td>18.2</td>
<td>16.0</td>
<td>25.4</td>
<td>n.s*</td>
</tr>
<tr>
<td>Down stream</td>
<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>pH</td>
<td>15-30</td>
<td>5.7</td>
<td>6.0</td>
<td>5.5</td>
<td>5.6</td>
<td>n.s*</td>
</tr>
<tr>
<td>OM (%)</td>
<td>15-30</td>
<td>2.2</td>
<td>2.5</td>
<td>1.8</td>
<td>2.2</td>
<td>*</td>
</tr>
<tr>
<td>P (mg/kg)</td>
<td>15-30</td>
<td>4.2</td>
<td>4.2</td>
<td>1.6</td>
<td>2.0</td>
<td>*</td>
</tr>
<tr>
<td>N (%)</td>
<td>15-30</td>
<td>0.16</td>
<td>0.21</td>
<td>0.16</td>
<td>0.13</td>
<td>*</td>
</tr>
</tbody>
</table>

*Significant at P<0.05, n.s* Not significant at P<0.05

Discussion
The effects of land use/cover change on the soil properties were dependent on the conversions of grasslands to agricultural land uses (sugarcane, maize, cassava and maize), perennial to annual crops, soil depth and watershed positions. In the 0-15cm soil layer, the major soil properties affected were soil nitrogen at the midstream and soil texture at both the midstream and the downstream, whereas in the 15-30cm soil depth, the major soil properties affected were organic matter, nitrogen and soil texture at both the midstream and downstream and on phosphorus at the downstream (P<.05). This collaborates with the findings of many other researchers (Tukahirwa, 2003; Pamela et al., 2005; Isabiry et al., 2007).
The effect on soil texture at both the midstream and downstream was mainly attributed to the continuous cultivation without external inputs increasing soil erosion which led to the selective loss or removal of soil texture fractions in Sio catchment. This is comparable to the findings made by Odada et al., (2004) and Isabirye et al., (2007) in the Lake Victoria basin. The soils were highly susceptible to erosion in the annuals, grasslands and valleys due to the observed decline in soil structure (coarse textured soils) and low infiltration rates (fine textured soils) attributed to the presence of organic matter that helped to stick the soil properties together. This also explains why the course textured soils were responsible for the higher clay fractions in the 15-30cm soil layer. However, this finding is in disagreements with the results made by Berhe et al., (2005) who noted that soil erosion improves the overall quality of the soil in the depositional basins and this increases the proportion of water-filled pore spaces that generally changes the redox potential and bioavailability of essential nutrients which retards the activities of soil microbial organisms resulting in the protection of SOC from decomposition. Important to note is that soil texture can be expected not to vary over time (Bormann, 2008).

The effect of land use/cover utilization on nitrogen in both the soil layers and the watershed positions was largely attributed to surface runoff and burning of biomass which reduced N stocks. This corresponds with the findings reported by Hartemink et al., (2008), Tukahirwa (2003) and Bekunda et al., (2002) to the cause that in eastern Uganda and western Kenya where soils are mainly light textured Ferralsols, 90% of the soils were limited by nitrogen. The observed burning of farm residues was responsible for the removal of organic material that protected the soil against erosion since some ash that contained plant nutrients were lost easily by wind and water erosion. This was also argued by Verchot et al., (1997) that surface runoff is a major transport mechanism for N losses. It transports much of the N from agricultural fields ranging from 8–80%. The variations in the nitrogen content with depth in all the watershed positions was probably attributed to nitrate leaching in the course textured soils which allowed water to move through the large cracks and channels leaving nitrate behind in the soil aggregates where little water movement occurred. However, it disagrees with the findings made by Francis et al., (2005) who noted that some cropping systems which relied normally on legumes fixed nitrogen and restored soil structure and did not necessity an application of nitrogen fertilizers. In addition, the high nitrogen content in the midstream was mainly caused by an application of fertilizers in the sugarcane and maize plantations.

The effects of land use/cover utilization on soil organic matter were mostly attributed to the effects of tillage practices and over cultivation. Similar observations were made by Tukahirwa (2003) and Pamela et al., (2005). Elsewhere in the northern Ghana Braimoh (2004) also reported that continuous cropping is responsible for the deterioration of organic matter. These practices depleted the land cover and led to the dramatic loss of organic matter due to surface run-off. The tillage practices especially the usage of tractors for cultivation loosened the soil particles and made them susceptible to the entrainment by water during the erosion processes. The humus was not relatively resistant to further breakdown and decomposition in the 0-15cm layer but then it moved downwards to the 15-30cm layer by means like leaching and macro fauna activity. This explains why organic matter decreased in the upper soil layer as the aggregates were disintegrated in the 15-30cm soil layer. These arguments are also reinforced by Khresat et al., (2008) that the decreases in organic matter are attributed to the reductions in the tree canopy cover. However, this disagrees with the findings made by Buschiazzo et al., (2004) that the mineralization of soil organic matter was lower below larger tree coverage, indicating that a lower organic matter content can be expected in such areas. Above and beyond, the effects of organic inputs on the soil physical properties depend on the residence time or quality and placement of the material, thus organic inputs that decompose slowly will have a greater and more durable effect on soil physical properties than high quality organic resides.

The effect on soil phosphorus in the downstream was mainly attributed to leaching which caused the soil phosphorus to vastly accumulate in the 15-30cm soil layer and burning. This coincides with the findings made by Bekunda et al., (2002) that in the recent analysis of soil samples from Eastern Uganda soils also showed P to be very low (0-8.5 mg kg-1; Bray I) in 70% of the sampled sites. Generally the results are also inline with the findings of Deborah (2001) to the cause that the long term soil phosphorus losses via; leaching and rapid sorption may be responsible for phosphorus variations in the tropics. The noted trash burning practices undertaken by the communities might also be responsible for the reductions in the available P to the atmosphere in smoke. Due to this, the
organic matter may have had little capacity to strongly fix phosphate ions in soil before the burning. In addition, the phosphorus which may have been deposited in the soil during the fire could have been lost through soil erosion by wind and water. This was worsened by the high sand content which allowed a higher rate of leaching as water percolated through the soil. Grasslands had the uppermost phosphorous content in the 0-15cm soil layer due to modest organic matter fixation in the soil. The undisturbed natural ecosystems usually contain enough phosphorus in the biomass and soil organic matters to maintain a substantial standing crop of grasses (Nyle, 2002). Phosphorus being a less mobile nutrient in the soils might have caused it to accumulate more in soils of the sugarcanes and maize where mineral fertilizers were applied especially in the midstream. However, this finding is in disagreement with the results of Allsopp (1999) who argued that the differences in phosphorus may also be affected by some shrubs (Galenia) which affects the nutrient cycle.

The no significant effects of land use/cover change on soil texture with soil depth were largely attributed to the continuous cultivation with out external inputs while the variations in soil pH are accredited to the presence of organic matter in the soil, which by clearing of natural vegetation caused accelerated organic matter decomposition, nitrate leaching and acidity production. In addition, the increase of soil pH with depth indicates an accumulation of carbonates with soil depth (Philip et al, 1993) and soils (Nayle, 2002) high in organic matter especially active fractions of organic matter were responsible for relatively low levels of phosphorous fixation. Subsequently, the conversions of land cover to cropland were associated with reductions in soil organic matter of the topsoil (Ross, 1993 and Singh, 1996).

Conclusion

The effect of the conversion of grasslands into agricultural fields induced changes in nitrogen for the topsoil (0-15cm) while in nitrogen, organic matter and phosphorous for the subsoil (15-30cm) in both mid and downstream sections of the watershed. However, in the soil management campaigns, priority should go the construction of soil erosion trenches to minimize the loss of soil nutrients followed by training the communities on sustainable organic farming for the maintenance of environmental health, limitations on the use of fire in land management and over cultivation without external inputs. Further research is also needed to develop farming systems that conserve organic matter and also improve the quality of organic matter, N, P and soil texture in the study area.

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Recycling of Agriculture and Animal Farm Wastes into Compost Using Compost Activator in Saudi Arabia

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Abstract: Saudi Arabia, as well as other countries in the Near East region, is characterized by erratic weather conditions, limited area of fertile arable lands, and with acute water shortage. Although agricultural residues (AGR) production in the region is huge (more than 440 million tons), most of these residues are either burned in the field or utilized in an inefficient way. Utilization of AGR as compost may contribute to expansion of arable lands through its use for reclamation of soil and reduce irrigation requirements. This study was conducted at Al Khalidiah farm, Riyadh, Saudi Arabia to assess compost production at large commercial scale using several types of agricultural and animal by-products with addition of a BZT®Compost Activator (based mainly on microorganism, enzymes and yeast). In this study, two types of compost piles were made at the farm. The first pile of compost was made of different agriculture residues, namely: animal wastes (quail, goat and sheep manure), brownian agricultural wastes (windbreaks residues, date trees, citrus and olive trees pruning) and green landscape grasses (50%, 25% and 25%, respectively) and was treated with a tested compost activator. The same agriculture residues combination was also made for the second pile as traditional compost (control or untreated compost) without the activator. The two piles were turned every 5 days; then moisture, temperature was checked and values were recorded every five days. Composite samples were collected regularly for testing chemical and biological parameters such as: nitrogen, potassium, organic matter, organic carbon, C/N ratio, heavy metals, total viable bacterial counts, yeast and molds, total coliform, fecal coliform and salmonella detection. The results showed a specific decrease in C/N ratio of compost activator treated pile to 15:1, combined with production of compost free of Salmonella, total coliform, fecal coliform, mycotoxins and heavy metals. The tested Compost Activator stimulates the composting process with concentrated bacteria and enzymes, the same bacteria and enzymes that occur in nature. This accelerated method provides good quality compost product in shortest time, as little as 35 days in comparison with 68-180 days for the traditional compost without activator materials (the traditional method). It could be concluded that the commercial compost product made from agriculture residues and treated with the tested compost activator is a safe alternative to chemical fertilizers and the best soil amendment that nature provides. These agricultural residues, when fully exploited could have an important role in bridging the food gap in Saudi Arabia.

Key words: agricultural residues, organic wastes, recycling, animal wastes, BZT® Compost Activator

Introduction

It is important nowadays to improve soil health by providing the much needed organic matter, least soil become impoverished. The scope and potential for recycling variety of resources in agriculture is vast by any standards. Agriculture wastes recycling can bring tremendous benefits to agriculture and land management in long run. In addition there are the benefits of a cleaner environment, a healthier habitat and an intelligent use of all available recyclable resources without condemning them as wastes. Towards this end agriculture solid waste compost could serve as a valuable organic matter source given the shortage of organic nutrient source (Prakash, et al., 2007).

Defining quality standards for organic agriculture and animal wastes is a very difficult task given the heterogeneity of residues that occur in farm wastes and processing methods adopted. Integrated nutrient management combining both inorganic and organics result in wholesome improvement of the soil. This can be done by adopting the technology of “composting” (Xi, et al.,

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The term composting refers to controlled biological decomposition process that converts organic matter to a stable, humus-like product. The process depends upon microorganisms which utilize decomposable organic both as an energy and food source. The composting process converts a material with potential odor and other nuisance problems into a stabilized product that is reasonably odor and pathogen free. In addition, the volume and weight of the composted product is less than that of the original raw waste because composting converts much of the carbonaceous material to gaseous carbon dioxide. Heat generated during the process destroys pathogenic organisms and weed seeds that might be present in the raw waste, and helps to drive off moisture. The degradation process takes place in the presence of air (aerobic) and results in elevated process temperature and the production of CO2, water and stabilized organic residue. The key feature of the composting process is the generation of heat by biological activity during the decomposition of the substrate materials. By forming the waste into large masses under appropriate conditions, they will reach high temperature, resulting in rapid degradation. More importantly, these temperature have a sanitizing effect upon the waste, reducing the numerous of pathogenic organism (Iyenger & Bhave, 2005).

Keeping in view, the benefits of farm organic agriculture and animal manure wastes as well as its inherent limitations such as analysis and slow action, a study was taken up to investigate the possibility of conversion of solid agriculture waste into enriched compost in short incubation time and to evaluate their nutritional quality.

The carbon: nitrogen ratio (C:N) affects the rate of biological activity. Carbon: nitrogen ratios of 15:1 to 35:1 are acceptable. If the C:N ratio is less than 25:1, organisms cannot utilize all of the nitrogen available, and nitrogen is then lost as ammonia. This, in turn, results in an unpleasant odor, possible air pollution, and loss of potential fertilizer value. When the C:N ratio exceeds 30:1, the rate of decomposition decreases. Green landscape wastes and animal manure can be mixed with the carbonaceous material to lower the C:N ratio to 30:1, or below (Nagavallemma, et al., 2004)

Temperature is a good indicator of biological activity in the compost pile, and is easily measured. Moisture content, oxygen availability, and microbial activity all influence temperature. Two or three days after organic wastes are mixed and placed in piles; thermophilic microbes should begin to dominate. These organisms prefer a temperature of 37.7 °C to 65.5 °C. As long as a pile temperature is increasing, it is functioning well and should be left alone. As the temperature peaks, and then begins to decrease, the pile should be turned to incorporate oxygen into the compost. After turning, the pile should respond to the mixing and incorporation of oxygen, and temperature should again cycle upwards. Ideally, the turning process should be continued until the reheating response does not occur again; indicating that compost material is biologically stable (Cayuela et al., 2004)

The main aim of this article is to speed up the natural composting process using BZT®Compost Activator. Break down organic waste to the best, safest fertilizer. Whether its grass, leaves and yard debris, agricultural manure and litter or industrial bio- solids, the natural way to solve this problem of organic waste build up is through short time composting using these microencapsulated bacteria and enzymes. Mother Nature can break organic wastes but it can take many months or years to accomplish. To Speed up this natural process, BZT®Compost Activator that contain identified strains of natural bacteria and enzymes was applied to obtain a finished compost in the shortest time possible.

Material and methods

Agriculture and animal samples preparation

The investigation on the biodegradation and recycling of agricultural wastes includes characterization of ingredients; composting and testing the components in the field was done at Al Khalediah Farm, Riyadh, and KSA. The main raw materials used for compost preparation were agriculture farm wastes and animal manure. Agricultural farm wastes include Brownian wastes such as windbreaks residues, date trees, citrus and olive trees pruning, and green landscapes such as landscape grass, vegetables and fruits. Agriculture solid wastes were sun dried and shredded to 1-2 inches using a Mourbark shredding Machine Animal manure was collected from the quail and sheep section.

Characterization of organic materials used for composting

The organic wastes collected from different sources were analyzed for pH, electrical conductivity, temperature, organic carbon, total nitrogen, total phosphorus, total potassium using
standard procedure (APHA,1992), and total micronutrients were analyzed by standard procedure given by (APHA,1992) using Atomic absorption spectroscopy.

Microbial activity and temperature measurements of Compost Piles

Piles compost samples were biologically analyzed during the composting process. Microbial analysis included total viable bacterial counts (cfu/g), molds and yeasts counts (cfu/g), total coliform (MPN/100g), fecal coliform (MPN/100g), salmonella detection (cfu) and mycotoxins detection by ELISA. Analysis was done according to (Jackson, 1973) and (Wong & Lin, 2002).

Biological treatments adopted for composting and composting methods

For the preparation of compost, followed the Turned Windrows method as per as (Fleming, 2001). Under this process the agriculture wastes were mechanically shredded to 1 -2 inches using a large scale USA Mourbark grinder machine (8 tons/h), cans and iron wastes were separated electromagnetically and then a good basic compost pile layered in browns, greens and animal manure or course and fine as a rule of thumb. The pile composting constructed ratio was 1:1:2 (brown: greens: animal manure, respectively). Piles mixed solid waste volume of 15 X 2.5 X 1.2 (Length x Width X Height) were used and the required operating condition of moisture, temperature, air were maintained throughout the composting as per as standard process (Hasen et al., 2001). Layers were alternated and each layer was inoculated by BZT®Compost Activator to aid the rapid decomposition. 29g of BZT® Compost Activator, a dry powder of microencapsulate bacteria and enzymes dissolved in 1.9L of warm water and sprayed regularly above all 0.9m x 1.2m x 0.3m high stack and mix systematically. N:P:K ratio was adjusted to 10:10:1 using Nitrovose fertilizer. Pile moist was kept and turned every 5 to 7 days. Homogenized samples were collected each 5 days intervals for microbial and chemical determinations. Pile temperature was monitored each 5 days through the center of the compost piles at different locations.

Results and Discussion

Organic matter recycling is a vital for supplementing plant nutrients and maintenance of soil productivity. Organic matter resources have therefore to be identified, characterized and utilized in the crop production practices suitably. Large quantities of agriculture and animal manure waste materials are originated from agriculture farms need to be evaluated to meet plant nutrient requirements.

Physical composition of agriculture and animal manure wastes

Agriculture waste composition was observed very demographically. Prior to segregation, the solid urban wastes consisted of some reusable material such as plastic, metals, glass and paper which totally constituted to about 10%. This was separated and further used in recycling industries. Agriculture matter and other decomposable is the predominant constituent which are present to an extent of 90%.

Chemical composition of organic wastes

The chemical compositions of various organic materials used for preparing the compost are given in Table 1. Agriculture waste includes brown (citrus old branches, palm leaves) is one of the potential organic carbon residues and low nitrogen residues , which on recycling yield valuable and nutrient moderate waste. The brown waste was found to be slightly acidophil in nature (pH 5.70) and was fairly low in N (0.96%), P (0.0018%), fairly rich in K (0.70%) and Ca (0.72%). The organic carbon was 39% with a C: N ratio of 40:1. Green leaves were rich in N (2%) and was used to supplement N to initially counter the nitrogen depletion and it had C:N ratio of 18:1. Animal manure used as an additive or inoculums for the compost treatments. This mainly served as a starter material for composting.

Data from the research showed that proportioning of mixed wastes had resulted to desirable C/N ratio (30:1) as generally agreed by many researchers (Sincero et al., 1996., Landerth & Rebers, 1996), moisture about 65% and temperature 60°C were maintained which had been recommended by other researchers for composting process(Tiwari et al., 1989., Diaz & Golueke, 1989, Davis et al., 1998).

It also enhances the decomposition of cellulosic plant material (Tiwari et al., 1989) and it had 2.5% N with a C: N ratio of 10:1. Also results explained that animal wastes were highly rich in Fe
(826 mg/kg), Cu (22 mg/kg) and Zn (152.60 mg/kg) when compared with brown and green leaves. Hazard heavy metals like Cd and Pb were found to be negligible in agriculture and animal wastes.

**Table 1. Chemical Composition of raw materials used for composting**

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>Brown</th>
<th>Green leaves</th>
<th>Animal wastes</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>5.70</td>
<td>6.2</td>
<td>7.00</td>
</tr>
<tr>
<td>Ec(μs cm⁻¹)</td>
<td>1445.000</td>
<td>1296.00</td>
<td>1363.00</td>
</tr>
<tr>
<td>Organic carbon (%)</td>
<td>39.00</td>
<td>36.00</td>
<td>25.00</td>
</tr>
<tr>
<td>Nitrogen (%)</td>
<td>0.96</td>
<td>2.03</td>
<td>2.50</td>
</tr>
<tr>
<td>Phosphorus (%)</td>
<td>0.0018</td>
<td>0.14</td>
<td>0.27</td>
</tr>
<tr>
<td>Potassium (%)</td>
<td>0.70</td>
<td>2.20</td>
<td>0.36</td>
</tr>
<tr>
<td>Calcium (%)</td>
<td>0.72</td>
<td>0.76</td>
<td>0.86</td>
</tr>
<tr>
<td>Nitrates (mg kg⁻¹)</td>
<td>1.60</td>
<td>0.75</td>
<td>0.11</td>
</tr>
<tr>
<td>Fe (mg kg⁻¹)</td>
<td>500</td>
<td>500</td>
<td>826</td>
</tr>
<tr>
<td>Cu (mg kg⁻¹)</td>
<td>6</td>
<td>14</td>
<td>22</td>
</tr>
<tr>
<td>Cd (mg kg⁻¹)</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>Zn (mg kg⁻¹)</td>
<td>22.60</td>
<td>38.80</td>
<td>152.60</td>
</tr>
<tr>
<td>Pb (mg kg⁻¹)</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>C : N ratio</td>
<td>40 : 1</td>
<td>18 : 1</td>
<td>10 : 1</td>
</tr>
</tbody>
</table>

**Chemical characteristics of the matured compost**

The data on chemical properties of the composted solid wastes are given in Table 2. The pH of the BZT®Compost Activator treatment and control treatment was neutral to slightly alkaline within the experimental time. This may be due to the natural buffering of the waste used. Highest pH was recorded in 15 and 25 days compared to others. The results in the present study concurred with the observation of (Diaz & Golueke, 1989) who reported that the agricultural compost was slightly alkaline in nature and had a marked buffering capacity. The composting process is relatively insensitive to the pH of its feedstock (Fleming, 2001). Finished compost generally ends up with a pH around neutral, usually between 6 and 8, according to tests performed on finished, stable compost (Diaz & Golueke, 1989). Therefore, properly cured compost is suitable for most plants, although certain acid-loving plants may need a lower pH (which can be attained by the addition of a supplement, such as sulfur). Both the percent of organic carbon and nitrogen varied between treatment intervals. The carbon content was lowest in matured compost (25-30 days) when compared to the initial treatment (0 days) which was due to the activity of BZT®Compost Activator. The N content was highest in matured compost when compared to the initial treatment. pH in mixed wastes was 6.5 and after starting up of the processes, increased to about 7.0 and in compost product reached to 7.95 in windrow which were accordance with (Markel, 1981).

**Table 2. Chemical properties of the composted materials**

<table>
<thead>
<tr>
<th>Times</th>
<th>BZT® Compost Activator</th>
<th>Control</th>
</tr>
</thead>
<tbody>
<tr>
<td>Days</td>
<td>pH</td>
<td>Organic C%</td>
</tr>
<tr>
<td>0</td>
<td>6.5</td>
<td>28.77</td>
</tr>
<tr>
<td>5</td>
<td>7.0</td>
<td>26</td>
</tr>
<tr>
<td>10</td>
<td>6.46</td>
<td>25</td>
</tr>
<tr>
<td>15</td>
<td>8.35</td>
<td>25</td>
</tr>
<tr>
<td>20</td>
<td>8.00</td>
<td>22</td>
</tr>
<tr>
<td>25</td>
<td>8.67</td>
<td>26</td>
</tr>
<tr>
<td>30</td>
<td>7.95</td>
<td>23</td>
</tr>
</tbody>
</table>

Data given in Table 3 recorded that enrichment of agriculture and animal manure wastes with BZT®Compost Activator yielded compost with high P content (0.68%), K (0.86%) and Ca (1%). The enrichment of compost with BZT®Compost Activator increased the decomposition rate, which may be due to availability of microencapsulated bacteria and enzymes essential for the increased decomposition activity and nutrients availability. From this investigation it can be stated that
enrichment of agriculture waste with animal manure and BZT® Compost Activator resulted in value added compost. According to (Radhakrishna et al., 1995) enrichment of compost with nutrients like P in the form of Nitrovos phosphate resulted in high value compost due to higher degree of decomposition. Also results recorded that the treatment with BZT® Compost Activator resulted in trace elements availability such Fe, Cu and Zn (2092 ppm, 20 ppm and 164 ppm for Fe, Cu and Zn respectively) which are totally matched with European standards.

Physicochemical analysis of compost from the point of view N, P, K, Organic Carbon, Organic matter and heavy metals (Cd, Fe, Cu, Zn, Ni and Pb) agreed with WHO criteria (World Bank. Integrated resource recovery, 1987) and USEPA. The data presented in table 2 showed that the windrows system was more effective for nutrients marinating. Considering the high volume of agriculture and animal wastes, aerobic composting may be considered as an important. It could be concluded that windrow system may be recommended for better method for recycling of agriculture and animal wastes.

Table 3. Major and heavy metals properties of the compost piles.

<table>
<thead>
<tr>
<th>Day</th>
<th>K%</th>
<th>Ca%</th>
<th>P (mg/kg)</th>
<th>Fe ppm</th>
<th>Cu ppm</th>
<th>Cd ppm</th>
<th>Zn ppm</th>
<th>Pb ppm</th>
<th>K%</th>
<th>Ca%</th>
<th>P (mg/kg)</th>
<th>Fe ppm</th>
<th>Cu ppm</th>
<th>Cd ppm</th>
<th>Zn ppm</th>
<th>Pb ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.93</td>
<td>0.86</td>
<td>0.0024</td>
<td>818</td>
<td>14</td>
<td>ND</td>
<td>61.4</td>
<td>ND</td>
<td>1.80</td>
<td>0.94</td>
<td>0.23</td>
<td>1824</td>
<td>20</td>
<td>ND</td>
<td>109</td>
<td>ND</td>
</tr>
<tr>
<td>5</td>
<td>1.56</td>
<td>0.60</td>
<td>-</td>
<td>3458</td>
<td>10</td>
<td>ND</td>
<td>165</td>
<td>ND</td>
<td>1.80</td>
<td>0.76</td>
<td>-</td>
<td>1992</td>
<td>24</td>
<td>ND</td>
<td>112</td>
<td>ND</td>
</tr>
<tr>
<td>10</td>
<td>1.76</td>
<td>0.68</td>
<td>-</td>
<td>2756</td>
<td>30</td>
<td>ND</td>
<td>141</td>
<td>ND</td>
<td>1.80</td>
<td>0.64</td>
<td>-</td>
<td>2858</td>
<td>34</td>
<td>ND</td>
<td>144</td>
<td>ND</td>
</tr>
<tr>
<td>15</td>
<td>1.98</td>
<td>0.64</td>
<td>-</td>
<td>3530</td>
<td>32</td>
<td>ND</td>
<td>160</td>
<td>ND</td>
<td>1.90</td>
<td>0.90</td>
<td>-</td>
<td>2252</td>
<td>18</td>
<td>ND</td>
<td>115</td>
<td>ND</td>
</tr>
<tr>
<td>20</td>
<td>0.56</td>
<td>0.56</td>
<td>-</td>
<td>2552</td>
<td>20</td>
<td>ND</td>
<td>168</td>
<td>ND</td>
<td>0.98</td>
<td>0.98</td>
<td>-</td>
<td>2308</td>
<td>22</td>
<td>ND</td>
<td>145</td>
<td>ND</td>
</tr>
<tr>
<td>25</td>
<td>0.86</td>
<td>0.60</td>
<td>-</td>
<td>3442</td>
<td>32</td>
<td>ND</td>
<td>163</td>
<td>ND</td>
<td>0.90</td>
<td>0.98</td>
<td>-</td>
<td>1854</td>
<td>22</td>
<td>ND</td>
<td>134</td>
<td>ND</td>
</tr>
<tr>
<td>30</td>
<td>1.00</td>
<td>0.68</td>
<td>2092</td>
<td>20</td>
<td>164</td>
<td>ND</td>
<td>0.94</td>
<td>0.94</td>
<td>0.002</td>
<td>1013</td>
<td>13</td>
<td>ND</td>
<td>98</td>
<td>ND</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Temperature and Biological characteristics

The data on biological and chemical properties of the composted solid wastes are given in Table 4. Biomass content (Total viable counts) showed a marked increase after 5 days and a marked decrease at the end product. Further more results showed that total coliform, faecal coliform, mycotoxins and salmonella detection dramatically decrease with the compost pile temperature rises.

Table 4. Temperature and biological properties of the processed composed material

<table>
<thead>
<tr>
<th>Treatment (BZT® Compost Activator)</th>
<th>Control</th>
</tr>
</thead>
<tbody>
<tr>
<td>Days</td>
<td>TVC (cfu/g) x 10^5</td>
</tr>
<tr>
<td>-----</td>
<td>-------------------</td>
</tr>
<tr>
<td>0</td>
<td>0.5</td>
</tr>
<tr>
<td>5</td>
<td>0.71</td>
</tr>
<tr>
<td>10</td>
<td>Nil</td>
</tr>
<tr>
<td>15</td>
<td>Nil</td>
</tr>
<tr>
<td>20</td>
<td>0.84</td>
</tr>
<tr>
<td>25</td>
<td>5.2</td>
</tr>
<tr>
<td>30</td>
<td>0.33</td>
</tr>
</tbody>
</table>

Achievement to maximum temperature (over 55 °C) in windrow systems in related times 10 days ensured hygienic characteristics of compost and destruction of pathogen and parasite according to WHO criteria 15 and USEPA regulations for PSRP and condition in windrows composting system, according to PFRP regulations of U.S.EPA (Davis, et al., 1998). Also data from this research showed that in the early stage of composting, characterized by a high content of easily degradable substrate, it could be expected that the microbial counts represents an higher percentage compared to the stabilized compost, were the substrate availability is greatly decreased. Furthermore, reference to the content of
the total coliform, faecal coliform and Salmonella was dramatically decreased with the compost pile temperature rises. The good correlation parameters measuring different aspects of the microbial pool could imply that all the parameters depend on a common factor such as the availability of easily degradable substrate. In the first stage of the composting process the more readily degradable substances such as sugars, fats, starch and proteins are rapidly consumed and degraded. With the ongoing process the cellulose, hemicellulose and other polymers are attacked and humifications occur in the residual organic matter (Chen, et al., 1997). Therefore, during the process there is a decrease of the substances more recalcitrant to microbial decomposition. It is probable that this substrate availability dynamics have a remarkable effect on the behavior of the size and activity of microbial diversity and enzyme activities in BZT® Compost Activator as it is a dry powder of microencapsulated bacteria and enzymes. Nevertheless the aim of the present work was not to study microbial dynamics in compost, but to investigate the useful application of microencapsulated bacteria and enzymes on the fastest degree of compost maturity and to be more economically in production.

**Conclusion**

The results of the study clearly indicate that the Biodegradation and recycling of agriculture wastes using microencapsulated bacteria and enzymes can be transformed to enriched composts within only 35 days. This is an important message of practical significance if adopted by urban farmers. Thereby the soil health and in turn the productivity of soil can be maintained for feature agriculture. This point gains importance given the fact that the quantum of cultivable land around KSA is fast dwindling. Therefore the essence of the present study is that the urban farmers in KSA and Arab countries should be motivated to practice agriculture and animal waste recycling through bioremediation measures.

**References**


Determination of 86 Pesticide Residues in Leafy Vegetables using gas Chromatography Mass Spectrometry

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Abstract: A multiresidue method is described for detection and determination of 86 compounds of pesticide residues which commonly used in the pest control programs for crop protection. Good sensitivity and selectivity of the method are obtained with limits of quantification 0.01 mg/kg in almost all cases. The method was applied very satisfactorily to routine analysis as a complement to traditional GC-MS method and finally, limit of detection were also 10-20 times lower than maximum residue levels (MRL) established by codex alimentarius commission. More than 500 samples from leafy vegetables have been collected from vegetables market (Riyadh Development Company) in Riyadh. Pesticide residues were detected in 24.69% of the total samples (140 from 567 samples) and pesticides concentration were higher than MRL in 104 samples.

Key words: Leafy vegetables; pesticides; residue analysis; GC-MS.

Introduction

The preservation of human health from exposure to pesticides residues in foodstuffs remains a major objective in kingdom of Saudi Arabia. Pesticides constitute a very important group of chemical compounds that have to be controlled due to their higher toxicity and widespread use agricultural practice for field and post-harvest protection. Indeed over 1000 compounds may be applied to agricultural crops in order to control undesirable moulds, insects or weeds. To ensure the safety of food for consumers, numerous legislations such as codex directives (CODEX committee on pesticide residues, 2003) have established maximum residue limits (MRLs) for pesticides in foodstuffs.

Pesticides residue analysis in agricultural commodities compared other organic trace analysis has some peculiarities: (i) a wide range of analyses, with different polarities, solubilities and at different concentrations levels, may be determined in the same sample; (ii) there is a wide range of commodities with different matrix effects in the determination of analysis due to different water and fat content and biochemical composition; (iii) certified reference materials (CRMs) are not available, Rosa, Rodriguez (2008).

Nowadays, multi-residue methods for analysis of pesticide residues in food stuff is considered as routine work in several laboratories which carried out using homogenization of the sample with an appropriate solvent (s), separation of the liquid portion of the sample from insoluble material, purification and clean up by florisil column followed by final chromatographic determination step. Organic solvents commonly used to extract pesticides residues in fresh fruits and vegetables are acetonitrile, petroleum ether (PE) and diethyl ether (AOAC official methods of analysis, 1995). An extensive clean-up of organic extraction is necessary to reduce adverse effects related to the quantification of residues such as the masking of residue peaks by co-eluted matrix component, the occurrence of false positives and/or the inaccurate quantitation.

Materials and Method

Reagents and equipments

All pesticides standard were obtained from (Riedel de Haen and Supelco). We prepared 1mg/ml stock solution of each by dissolving 20mg of the pure analytical standard in 20 mg of acetone. A single composite standard solution was prepared by diluting with acetone according to limit of detection (LOD). All standard solutions were stored in glass-Stoppard flasks at 4°C. Mixed compound calibration solutions were prepared in acetone and they were used as spiking solution. Solvents (residue analysis grade) used were acetone, acetonitrile, petroleum ether and other reagents such as

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sodium chloride and anhydrous sodium sulphate, florisil 60-100 mesh for residue analysis were also from purchased from (Fluka). The florisil and anhydrous sodium sulphate was activated at 100°C over night and stored in 500 ml glass flask with glass stoppers and stored in oven at 100°C. The equipments used included a high-speed blender with a stainless steel jar (waring, USA), a shaking separation final (GFL, Germany), a rotavapor, R 215 and cooler circulator chiler B-740 (Buchi, Switzerland), Buchner funnel and chromatographic tubes with Teflon stopcocks and course fritted glass (Agilent, USA) and syringes (Hamilton Bonadus AG, Switzerland). All glassware were rinsed thoroughly using soap and deionization water, then washed with acetone and dried in oven (100-130 °C) over night.

Samples collection
This study was conducted during two years from January 2007 to December 2008. More than 500 leafy vegetables samples (rocket, lettuce, coriander, corchorus, cabbage, parsley, basil, spinach, radishes dill, mint, green onion, chard and leek) have been collected from Al-tamer vegetables market in Riyadh. Samples were put in sterile polythene bags and transported to the laboratory where they were analyzed immediately or stored at 4°C until analysis within 24h.

Sample Preparation, Extraction and partitioning
The chopped leafy vegetable samples (100g) were placed in a stainless steel jar 1L and extracted with 200ml of acetonitrile and 10g celite, the blender was vigorously homogenized into high speed for 2min and the mixture was filtrated by using Buchner funnel fitted with shark-skin filter paper into 500ml suction flask. An aliquot of organic was transferred to 1L separator funnel and added 100ml of (PE), the mixture was vigorously shaken for 1-2 min and then was added 100ml saturated solution of Nacl and 600 water. The mixture was vigorously mixed and the separator funnel was allowed to be held at horizontal position for few minutes. The aqueous layer was discarded and the solvent layer was washed with twice time 100ml portions of distilled water and the washed layer were transferred into 100ml beaker and washed with 15g of anhydrous sodium sulphate. Finally the extract was concentrated to 5ml volume and transferred directly to florisil column.

Florisil column cleanup
Florisil column cleanup was conducted according to the AOAC method (1995, chap. 10). The column was peppered containing about 12cm activated florisil topped with 1cm anhydrous sodium sulphate, column was washed by 40ml (PE) and than was added extract concentrated to 5ml and was allowed to pass through the column. The walls of the tube were rinsed additional small portions of petroleum ether and elute at 5ml/min with 200ml 6% eluting solvent (Diethyl ether in (PE)), and then 200ml 15% and finally 200ml 50% eluting solvent (Diethyl ether in (PE)) at 5ml/min.

Chromatographic instrumentation and quantification
Gas chromatograph-mass spectrometer (Aglient model 6890N) gas chromatograph coupled with (model 5975B) quadrupole mass spectrometer with a GC column HP-5MS 5% phenyl - 95% methyl siloxane, 30m x 0.25mm id x 0.25 μm film thickness. GC operating conditions: splitless injection, injector temperature 250 °C, helium carrier gas (99.9999 purity) at flow rate 0.9 ml/min with column head pressure 7.4 psi, oven temperature from 70 °C (2 min hold), than raised to 130 °C at the rate (25 °C/min) afterwards raised to 220 °C at (2 °C/min) and than raised to 280 °C at (10 °C/min) and eventually (4.6 min hold). The sample (1µL) was injected in splitless modes. The MS system was routinely set in selective ion monitoring (SIM) mode and each compound was quantiaited based on peak area using one target and one or two qualifier ion. Mass spectrometer parameter was set as follows: electron impact ionization mode with 70 eV electron energy, scan mass range 100-400 at 0.62 sec/cycle. Ion source temperature 230 °C, MS quad temperature 150 °C, EM voltage 1450 and solvent delay 4 in.

Results and Discussion
A multiresidue procedure was carried out to monitoring the pesticide residues in a wide range of the most common consumed leafy vegetables samples collected from the central market located in Riyadh, Saudi Arabia during two years, i.e. 2007 – 2008. The analyzed samples composed of fourteen
species of leafy vegetables, i.e. rocket, lettuce, coriander, corchorus, cabbage, parsley, basil, spinach, radishes, dill, mint, green onion, chard and leek. A wide range of pesticide residues were detected and quantified in the analyzed samples during the two years of this study. In 2007 it was detected the residues of 24 pesticides while in 2008 it was detected the residues of 27 pesticides.

Data in Table (1) shows the amounts of the detected pesticide residues in leafy vegetable samples collected from different locations in Saudi Arabia during the year 2007. According to the detected pesticides, it is clear that there are a wide range of compounds which included insecticides (25 compounds), herbicides (three compounds, i.e. linuron, chloroneb and amitraz) and fungicides (one compound, i.e. teradifon). In case of the detected insecticide residues which represent the majority of the detected compounds, it was found that such insecticides could be classified chemically into their major four chemical groups, i.e. organochlorines, organophosphorus, pyrethroids and carbamates. The detected organochlorines substances were four insecticides, i.e. lindane, chlordane, mirex and endosulfan while the organophosphorus insecticides included seven agents, i.e. chloropyrifos, mevinphos, azinophos-ethyl, phosmet, ethoprophos, diazion and iprobenfos. As for pyrethroids, it was detected eight compounds included tetramethrin, permethrin, deltamethrin, lambda-cyhalothrin, cyfluthrin, allethrin, fenvalerate and resmethrin. For carbamates, only two compounds were detected, i.e. bendiocarb and fenoxycarb. The mentioned pesticides were detected in fourteen leafy vegetables, included rocket, lettuce, coriander, corchorus, cabbage, parsley, basil, spinach, radishes, dill, mint, green onion, chard and leek.

Actually, according to the detected pesticides in and/or on the leafy vegetables involved in this study, it was observed that total numbers of the detected compounds were found in rocket followed by parsley, mint, green onion, lettuce, leek, corchorus, spinach, coriander, dill, radishes, cabbage, basil, and chard. The total number of the detected compounds in such leafy vegetables was 9, 7, 5, 5, 4, 4, 4, 3, 3, 3, 3, 2, 2, 1 compound, respectively.

Depending on the detected amounts of pesticide residues, the leafy vegetables could be ranked in descending order as follows: rocket, cabbage, green onion, radishes, corchorus, coriander, parsley, mint, dill, spinach, lettuce, basil, leek and chard which represent the lower leafy vegetable contained pesticide residues. In term of figures, the sum of the detected pesticide residues in such leafy vegetables were 0.933, 0.534, 0.338, 0.197, 0.178, 0.172, 0.158, 0.132, 0.128, 0.101, 0.081, 0.061, 0.034 and 0.002 ppm respectively. From such ranking, it was observed that rocket, cabbage and green onion were the most contaminated leafy vegetables.

In addition, when the frequency of the detected pesticide residues was calculated in the analyzed leafy vegetables, it was found that the most frequent compounds was permethrin followed by resmethrin and linden, endosulfan, iprobenfos, cyfluthrin, and phosmet. In term of figures, the frequencies for these pesticides were 9, 5, 5, 5, 4, 3, 3, 2, 2, and 1 respectively. The other detected compounds were frequented between two and one time. From the presented results it could concludes that rocket, cabbage and green onion were the most contaminated leafy vegetables, and the pyrethroids are the most frequented pesticides during the year of 2007.

As for the agriculture season of 2008, data represented the detected amounts of pesticides residues in leafy vegetables collected during the season of 2008 are listed in Table (2). The detected pesticide residues in the collected leafy vegetables samples were slightly differed from those presented in 2007 season (Figure 1). For example, in 2008 season, it was found the o,p'-DDT as organochlorine compound, phonophos, comaphos, phosphamidon, pirimiphos-ethyl, and dimethoat as organophosphorus, cypermethrin as pyrethroids. Also, it was detected thiobencarb, carbofuran, propamocarb as carbamates insecticides. As for fungicides, it found benomyl only. As for the detected amounts, it is clear that cyfluthrin represented the highest amounts of the detected residues which ranged between 0.25 to 0.58 ppm while the other detected concentrations were ranged between 0.01 to 0.0002 ppm. Overall, the pesticides residues were found in this study were approximate similar to other studies (Rosa & Rodriguez, 2008; Amoh & Drechsel, 2006; Dogheim & Ashraf, 2004).

In addition, based on the number of the detected residues, the leafy samples could be ranked in descending order as follow rocket, parsley, basil, green onion, coriander, dill, mint, corchorus, cabbage, lettuce, spinach, radishes, chard, and leek. The detected number of compound residues was 7.0, 5.0, 5.0, 5.0, 4.0, 4.0, 4.0, 3.0, 3.0, 2.0, 2.0, 2.0 and 1 respectively. As for the detected amounts of the mentioned pesticides, the ranking of leafy samples becomes different to be rocket is

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Table 1. Detected pesticide residues in leafy vegetable samples collected from different locations in Saudi Arabia during 2007.

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<tr>
<th>Pesticide</th>
<th>Rocket</th>
<th>Lettuce</th>
<th>Coriander</th>
<th>Corchorus</th>
<th>Cabbage</th>
<th>Parsley</th>
<th>Basil</th>
<th>Spinach</th>
<th>Radishes</th>
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<th>Mint</th>
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Table 2. Detected pesticide residues in leafy vegetable samples collected from different locations in Saudi Arabia during 2008.

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<td>0.023</td>
<td>0.04</td>
<td>0.524</td>
<td>0.661</td>
<td>0.076</td>
<td>0.273</td>
<td>0.263</td>
<td>0.61</td>
<td>0.149</td>
<td>0.18</td>
<td>0.253</td>
<td>0.131</td>
<td>0.0172</td>
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the most contaminated leafy samples followed by radishes < corchorus < green onion < basil < spinach < mint < chard < parsley < cabbage < coriander < lettuce < leek. In term of figures, the total detected amounts are 0.664, 0.61, 0.524, 0.391, 0.273, 0.263, 0.18, 0.149, 0.133, 0.076, 0.061, 0.04, 0.023 and 0.0172 ppm. for the mentioned leafy samples, respectively. In case of the frequencies of pesticide residues between the collected leafy samples, it was observed that dimethoat was the most frequented compound followed by cyfluthrin followed by cypermethrin which their frequencies were 50, 4.0 and 3.0, respectively. The other detected compounds were frequented between two and one time. However, the presented data of 2008 season clearly shows that rocket samples were the most contaminated leafy vegetables followed by radishes followed by corchorus and green onion while both of leek and chard were the lowest contaminated leafy samples. When data of the detected amounts of residues during the two mentioned seasons, i.e. 2007/2008 were compared with that MRL values, it could calculated the average of percentage of leafy vegetables samples contained amounts of residues exceeds the MRL values as listed in Table (3) and illustrated in Figures (2 and 3). From such data, it is clear that the majority of the analyzed leafy samples collected in 2007 contained exhibited higher values than those of 2008 except seven leafy vegetables, i.e. cabbage, basil, spinach, radishes, green onion, chard and leek which were higher in their values than those of 2007. In addition, when the analyzed samples distributed between the four mainly season of each year, i.e. winter, spring, summer and autumn (based on the analyzed date), neither correlation nor trend could be observed between the pesticide residues content and the mentioned season. The selected plant foods will not give for adverse biological effects to take place providing the residues of pesticides are controlled to be kept to a minimum. Pesticides residue monitoring programs should then be implemented to assure the minimum allowable residue levels in plant foods, especially with regards to permethrin, endosulfan, dimethoat (Rial-Otero, 2005).

According to the obtained results of the detected amounts of pesticide residues in the selected leafy vegetables, it is therefore clear that patterns of pesticide use are crop dependent: the predominant use of pesticides in leafy vegetables is mainly to control a wide range of lepidopteran larvae. In addition, the most reasonable explanation for the highly detected pesticide residues in rocket, cabbage and radishes may be due to the intensive

<table>
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<th>2008</th>
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<td>Rocket</td>
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<td>25.00</td>
</tr>
<tr>
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<td>0.00</td>
<td>0.00</td>
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<tr>
<td>Spinach</td>
<td>0.00</td>
<td>0.00</td>
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<tr>
<td>Radishes</td>
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<td>0.00</td>
</tr>
<tr>
<td>Corchorus</td>
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</tr>
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<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
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<td>0.00</td>
</tr>
<tr>
<td>Chard</td>
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<td>0.00</td>
</tr>
<tr>
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<td>0.00</td>
</tr>
<tr>
<td>Mint</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>Coriander</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>Lettuce</td>
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</tr>
<tr>
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</tr>
<tr>
<td>Summer</td>
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</tr>
<tr>
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<tr>
<td>Autumn</td>
<td>0.00</td>
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</tr>
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</table>
use of insecticides and the highly deposited amounted of the applied compounds on the broad leafs of such vegetables. Overall, insecticides found in this study were similar to those found in other studies (Amoah, et al., 2006; Cabras & Conte, 2001; Dogheim, et al., 2004; Gebara et al., 2005; Poulsen & Andersen, 2003). However, according to the detected amounts of the mentioned insecticides in these important leafy vegetables, make the necessary to continuing the pesticide residue monitoring programs which must be implemented to assure the minimum allowable residue levels in plant foods. In addition, the obtained results clearly indicate the actual situation of the misuse of insecticides which may affect in turn at long period the consumers' health.

![Figure 1](image1.png)

**Figure 1.** Total amount of the detected pesticide residues in the collected leafy samples during the two seasons, 2007-2008

![Figure 2](image2.png)

**Figure 2.** Percentage average of the leafy samples exceeds MRL values during 2007 and 2008.

![Figure 3](image3.png)

**Figure 3.** Percentage average of leafy samples exceeds MRL values in relation to the collection season.
Acknowledgement: The authors deeply thank Dr. Khaled Al-dughaither, general manager of Al-Riyadh development company; Mr. Ahmed Al-kanhal, assistant general manager; Engineer Abdalla Elktherai, manager of Al-Tameer vegetables and fruits market and assistant manager Abdulhakeem Al-Khamis for kin helps with financial and incorporeal support during this work.

References


Mathematical Modeling of Technological Parameters of the Work of Bucket Wheel Excavators SR, 1300

Ahmet Bytyçi*, Nexhmi Krasniqi

Faculty of Mining and Metallurgy, University of Pristina, Kosovo

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Abstract: This paper presents the results of research into the dependency between the technical and technological parameters of bucket wheel excavators in operation on the marly clay formations of surface coal mines in Kosova, according to analysis and design of experiments models that use first order $2^k$ orthogonal plans incorporating many factors. These types of computer simulation models were presented in such a way that perpetuated the dependence of the exponential equation for each parameter with the interpretation of a 3D graphics application module- MATLAB.

Keywords: Excavator, technological parameters, design of experiments, mathematical modelling.

Introduction

Where there is insufficient theoretical knowledge available, scientific research and the practice of the extraction of minerals in surface mines with continuous operations have shown that design of experiments models provide the best means of improving our understanding of surface mining processes. The effectiveness of continuous operations in the surface excavation of minerals depends on the degree of harmonisation between the technical parameters of the process and the geomechanic parameters of the formations that are being excavated (Lepojević, 1982). Design of experiments models using first order $2^k$ orthogonal plans can assist in the study of, and the optimisation of such excavation processes.

These models must include a balance between these parameters and need to incorporate a number of variables which characterise these processes, in a regression analysis. Such models can also be applied to the working processes of bucket wheel excavators SRs 1300 to study the working conditions in the excavation of over-burden in the surface mines of Kosova, to optimise the capacity per hour, “Qh”, and a number of other technical parameters, after overhauling the whole system. This method of researching the relationship between technical and technological parameters is relatively new in this field, and offers the possibility of expanding the spectrum of parameters studied and creates the opportunity to include a greater number of scientific arguments in the model, which allow us to describe the processes more objectively and accurately.

Design of experiments models

Design of experiments models using first order $2^k$ orthogonal plans can be used to investigate the relationship between technical and technological parameters, and can be used to increase the capacity coefficient and reduce the consumption of, or loss of electricity. This provides a good opportunity to build mathematical models which express the dependency between the technical and technological parameters in the working conditions (Makar, 1990) in excavating the marly clay formations of surface mines in Kosova. The clay formations of Kosova coal basins differ from the formations of other coal basins in their physical and mechanical features, in particular in the specific resistance to cutting, having taken in to consideration differences in the equipment used (20-130) daN/cm (Bytyçi, 2008). The purpose of our study was to determine the dependency of technical and technological parameters in unison at the point of optimisation of capacity per hour, “Qh”, for actual working conditions in marly clay formations before and after the overhaul of the whole system of continuous mining operations. In this context, the relationship between the technical and technological parameters is arrived at with expression (1)

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\[(Q_h,N,e,k_L) = f(S,h,v_k),\]  \(1\)

where:
- \(Q_h\) - capacity per hour \((\text{m}^3/\text{h})\)
- \(N\) – active power of the working wheel \((\text{kW})\)
- \(e\) – specific consumption of electricity \((\text{kWh/m}^3)\)
- \(k_L\) – specific resistance to cutting \((\text{daN/cm})\)
- \(S\) – thickness of the cut piece \((\text{m})\)
- \(h\) – cutting height \((\text{m})\)
- \(v_k\) – speed of the working arm \((\text{m/min})\)

Function (1) can be transferred in expression (2)

\[
R = C \Pi^{\prod_{i=1}^{k} f_i^{p_i}}, \quad (2)
\]

which is composed of \(R\{Q_h,N,e,k_L\}\), where the unknown \(C\) and \(p_i\) can be found by statistical analysis of the results, where “\(N\)” number of tests were undertaken. Starting from the fourth principle of the work process of continuous operations (Živković, et al, 2002), our research is based on three variable parameters: the thickness of the cut piece, “\(S\)”, the cutting height, “\(h\)” and the speed of the working arm movement, “\(v_k\)”, see Figure 1.

![Figure 1 Technological parameters (Makar, 1990)](image)

The number of tests will be:

\[
N = 2^k + n_o, \quad (3)
\]

where:
- \(k\) – number of parameters \(k = 3\)
- \(n_o\) - the number of tests at the centre of computer simulation model \(n_o = 4\)

\[
N = 2^3 + 4 = 12 \quad \text{proof}
\]

The easiest way to show the results of the research, measuring the capacity per hour “\(Q_h\)” of bucket wheel excavators and other parameters such as active power of the working wheel, “\(N\)”, specific consumption of electricity, “\(e\)”, and the resistance to cutting in the marly clay formations “\(k_L\)”, is to set up a matrix computer simulation model in which we pre-programme the variables (\(S, h, v_k\)) with values (-1.0, +1). Programming or transformation of real values is done according to expression:
\[ x_i = 1 + 2 \frac{\ln f_i - \ln f_{\text{max}}}{\ln f_{\text{max}} - \ln f_{\text{min}}}, \] (4)

where:
- \( f_i \) – average value
- \( f_{\text{min}} \) – minimum value
- \( f_{\text{max}} \) – maximum value

When \( f_i = f_{\text{max}} \), the standard value will be:
\[ x_i = +1, \]
and when \( f_i = f_{\text{min}} \) the standard value will be \( x_i = -1 \). The design of experiments model matrix is presented for real and standard values of technological parameters in Table 1, which represent:
-1 - lower limit value
0 - average value
+1 - upper limit value

Order of the implementation of the research is done spontaneously and randomly (mixed) to avoid eventual errors (Kedhi, 1984). Before beginning the research into the dependency of the above mentioned parameters when measuring the capacity of the bucket wheel excavator, we must decide on initial values in the computer simulation model, which represent the average values of the parameters in the verification procedure of SR,1300 excavator capacity. Upon verification of the capacity of this excavator, a total 40 measurements were realised, according to the manufacturer’s technological specifications, which guarantees a capacity of 1300 m³/h which can be achieved with the following average levels for the parameters listed below:

- Thickness of the cut piece \( S = 0.35 \) m
- Cutting height \( h = 4 \) m
- Working arm speed \( v_k = 19 \) m

Because in our case the parameters were not given, we can choose our own steps of investigation, however we have to take into consideration that the parameters that have a big affect on the process require us to take small step, whereas the parameters that have a small affect require us to take large steps (Montgomery et al., 1994). Thus following this principle, the set out steps of parameters are:

- Thickness of the cut piece \( h_1 = 0.15 \) m
- Cutting height \( h_2 = 1 \) m
- Working arm speed \( h_3 = 1 \) m/min
the parameter limits in our case are
- Thickness of the cut piece
- lower limit \( S = 0.2 \) m
- upper limit \( S = 0.5 \) m
- Cutting height
- lower limit \( h = 3 \) m
- upper limit \( h = 5 \) m
- Speed of working arm
- lower limit \( v_k = 18 \) m/min
- upper limit \( v_k = 20 \) m/min
Table 1. Design of experiments model matrix $2^k+n_0$

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<thead>
<tr>
<th>Nr</th>
<th>Real variables</th>
<th>Programmed variables</th>
<th>$y_i$</th>
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<td>$S$ $h$ $v_k$ $X_0$ $X_1$ $X_2$ $X_3$</td>
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</tr>
<tr>
<td>1</td>
<td>0.20 3 18 +1 -1 -1 -1</td>
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<td>0.50 5 20 +1 +1 +1 +1</td>
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**Measurement of technical parameters**

The values of the technical parameters were determined using two methods: by direct measurement and by analysis. We used the direct measurement method to measure capacity per hour, “$Q_h$”, and active power, “$N$”, and by analysis we determined values for the following energy parameters: the specific consumption of electricity “$e$”, and the specific resistance to cutting “$k_L$”. The capacity per hour “$Q_h$” was measured using the scale: MULTIBELT Weighers 2BMP + Integrator Ramsey Micro-Tech 3000 (Fig. 2) and the active power of the working wheel unit was measured using the measuring instrument METREL “MI 2292 Power Quality Analyser Plus” (Fig. 3).

**Figure 2.** Measuring capacity of excavator MULTIBELT Weighers 2BMP+Integrator Ramsey Micro-Tech 3000

**Figure 3.** Measurement of the active power of the working wheel unit with the MI 2292 Power Quality Analyser
As set out above, the group of parameters that were determined by analysis were: the specific consumption of electricity, “e”, and the specific resistance to cutting “kL”. Specific consumption of electricity, “e”, expresses the quotient of the active power of the working wheel unit and the capacity per hour achieved by the excavator in this instance.

\[ e = \frac{N}{Q_{ef}} \text{ kWh/m}^3, \]  

\( N \) – active power \( \text{kW} \)
\( Q_{ef} \) – excavation capacity per hour \( \text{m}^3/\text{h} \)

**Table 2. Technical parameters obtained by measurement**

<table>
<thead>
<tr>
<th>Nr</th>
<th>Parameters investigated “yi”</th>
<th>( Q_{h,m} \text{m}^3/\text{h} )</th>
<th>( N \text{ kW} )</th>
<th>( E \text{ kWh/m}^3 )</th>
<th>( kL \text{ daN/cm} )</th>
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</table>

Specific resistance to cutting “kL” is defined by the following expression (Zivković et al, 2002)

\[ kL = \frac{5540 \eta S - QnD/\rho}{69.25 \sqrt{\frac{Q3}{Dn_{eb} \phi}}} \text{ daN/cm} \]  

where:
\( \eta \) - rate of usage of electromotors
\( D \) - Diameter of the working wheel \( \text{m} \)
\( \rho \) – density of the formation \( \text{t/m}^3 \)
\( g \) – gravity \( \text{m/s}^2 \)
\( n_{eb} \) – number of bucket unloads \( \text{unload}^{-1} \)
\( \phi \) – angle of excavation \( \text{o} \)

**Results**

Mathematical analysis of the results of the research was done with the aim of building mathematical models which express the nature of the interaction between the technological and technical parameters of the working bucket wheel excavator during the excavation of marly clay formations. In this case, the mathematical models are built on a platform of linear regression (Wackerly et al, 1996).

\[ y = b_0 + \sum_{i=1}^{n=3} b_i x_i \]  

where:
\( b_i \) – coefficient of the unknown
\( x_i \) – unknown
then its approximation factors include: thickness of the cut piece, "S", cutting height, "h", and the speed of movement of the excavator’s working arm “vk”. Connecting the parameters listed above with those of the regression platform is done with: \( x_1=S, \) \( x_2=h \) and \( x_3=v_k \), where in this case the regression platform \( y=b_0 + b_1 x_1 + b_2 x_2 + b_3 x_3 \) must be transformed into the logarithmic function

\[
\ln R = \ln C + p_1 \ln S + p_2 \ln h + p_3 \ln v_k ,
\]

Variables that make up the logarithmic function (9) are:

\[
\begin{align*}
y &= \ln R \\
x_1 &= \ln S \\
x_2 &= \ln h \\
x_3 &= \ln v_k
\end{align*}
\]

coefficients of the unknown are replaced with the transformation equations:

\[
\begin{align*}
b_0 &= \ln C \\
p_1 &= b_1 \\
p_2 &= b_2 \\
p_3 &= b_3
\end{align*}
\]

in these conditions the regression platform takes the form of an exponential function

\[
R = C S^{p_1} h^{p_2} v_k^{p_3} ,
\]

where: \( C \) – constant

\( p_1, p_2, p_3 \) – exponents

According to expression (3) and from the values of \( x_i \) variables, the computer simulation model matrix is formed as \( 2^k+n_0 \), where \( k=3 \). Based on the properties of the orthogonal which satisfy the matrix, the coefficients of the regression analysis equation “b” will be determined by expression

\[
b_i = \frac{1}{N} \sum_{u=1}^{N} x_{iu} y_u ,
\]

where:

\( N \) – number of tests

\( x_{iu} \) – value of factor in the test u-te

\( y_u \) – value of function in the test u-te

Coefficient of the regression analysis platform (mathematical model) based on the conditions laid down and the transformation of the equation in the initial state is done under expression:

\[
p_i = \frac{2b_i}{\ln \left( \frac{p_{\text{max}}}{p_{\text{min}}} \right)}
\]

\[
p_0 = \sum_{n=1}^{3} \sum_{i=0,1,2,3} \frac{1}{n!} \frac{1}{i!} \left( \frac{\sum_{i=0}^{n-1} \sum_{i=1}^{n} \text{p}^{\frac{1}{i}} \text{f}_{\text{max}} }{\sum_{i=0}^{n-1} \sum_{i=1}^{n} \text{p}^{\frac{1}{i}} \text{f}_{\text{min}}} \right)
\]

in this instance we obtain correlation between the technical and technological parameters which can be determined with equation (2). Evaluation of the regression analysis platform parameters is usually done under criterion F, in comparison with dispersion from point zero

\[
F = \frac{\sum_{i}^{2} \frac{S_i}{S_i^2}}{\sum_{i}^{2} \frac{S_i}{S_i^2}} > F^* ,
\]

Dispersion of the values of model parameters is set according to the relationship
\[ S_i^2 = \frac{s_i^2}{f_i} \]  

(14)

\[ F - \text{calculated value} \]
\[ F^* - \text{value from the table for given conditions} \]
\[ (f_{1S}=1 \text{ and } f_{E}=3) \quad F^* = 10.13 \]
\[ s_i^2 - \text{dispersion of correlation parameters} \]
\[ S_E^2 - \text{dispersion of results at point zero} \]
\[ f_i - \text{degrees of tolerance} \]

while the sum of exponents is calculated

\[ S_{bi} = b_i \sum_{n=1}^p x_n y_u = N b_i^2 \]  

(15)

where \( i=0,1,2,3 \) in this instance:

\( i=0 \quad N=12 \)
\( i=1,2,3 \quad N=8 \)

In this instance, we set the degrees of tolerance “\( f_i \)”, whilst the dispersion is calculated by expression:

\[ S_E^2 = \frac{S_E}{f_E} \]  

(16)

where:

\[ S_E - \text{sum of exponentials} \]
\[ f_E - \text{degrees of tolerance} \]

The dispersion at point zero in this case is calculated according to the expression (Montgomery et al., 1994)

\[ S_E^2 = \sum_{u=1}^4 y_u^2 - \frac{1}{n_o} (\sum_{u=1}^4 y_u \sum_{u=1}^4 y_u)^2 \]  

(17)

The degrees of tolerance in this case is calculated using expression \( f_E=n_o-1 \). In the case when the level of significance is “\( \alpha \)” and \( F_l>F^*_t \), parameters “\( b_i \)” must have values, otherwise these parameters must be excluded from the mathematical model. Any mathematical model which describes the working processes of a system or an emerging phenomena must determine a confidence interval according to criterion “\( F \)”, for significance level “\( \alpha \)”.

\[ F_l<F^*_t \]  

(18)

As the central point lies in the same plane in which the experiment is repeated \( n_o \) times, the estimated value of criterion -\( F_l \) needed to determine the confidence interval of the mathematical model is expressed in equation below.

\[ F_{lr} = \frac{S_M^2}{S_E^2} \]  

(19)

Difference in the distribution of values of the experiment \( y_i \) and of the calculated values \( \hat{y}_i \)

\[ S_M^2 = \frac{1}{F_{1S}-F_E} \left\{ \sum_{s=1}^{12} \left( y_s - \hat{y}_s - \frac{1}{n_o} (\sum_{u=1}^4 y_u \sum_{u=1}^4 y_u) \right)^2 \right\} \]  

(20)

whereas the results of measurement with the medium level is calculated according to expression:

\[ S_M^2 = \frac{1}{F_E} \left\{ \sum_{u=1}^{12} y_u^2 - \frac{1}{n_o} (\sum_{u=1}^{12} y_u)^2 \right\} \]  

(21)
therefore the values from the table according to criterion “F” are solved prior to the respective tables at
the degrees of tolerance, where in our case $F^*_1 = 9.01$

$$f_{LE} = f_{RF} + f_{E}$$

(22)

and

$$f_{E} = n_{0} - 1$$

Applied procedures of dispersive and regressive analysis were undertaken and dependencies found
by analysing the technological parameters which define technical parameters, carried out during the
phase determining the capacity per hour “$Q_h$”, which in this case allowed us to determine the correlation
between the parameters individually. From equation (2) we may derive equations for the dependencies
of technological and technical parameters, such as: capacity per hour, “$Q_h$”, active power RRRP, “N”,
specific consumption of electricity “$e$” and specific resistance to cutting, “$k_L$”. Graphical 3D
interpretation of the dependencies of technological and technical parameters was carried out individually
for each instance in MATLAB (Bytyçi, 2008).

- Capacity per hour

$$Q = 92 S^{0.958} h^{0.896} v_k^{0.908}$$

- Active power

$$N = 0.128 S^{0.691} h^{0.634} v_k^{2.722}$$

- Specific consumption of electricity

$$e = 0.00139 S^{-0.267} h^{-0.262} v_k^{1.83}$$

- Specific resistance to cutting

$$k_L = 0.0493 S^{0.948} h^{0.4504} v_k^{2.589}$$

The following are graphical interpretations of correlations obtained when cutting height $h=4$ m

Figure 4. Regressive analysis surfaces of dependencies of capacity per hour, “$Q_h$”, the thickness of the
cut piece, “S” and the speed of the working arm, “$v_k$”

Figure 5. Regressive analysis surfaces of the dependencies of active power “$N$”, from the thickness of
the cut piece, “$S$”, and the speed of the working arm “$v_k$”
Following on from regressive analysis platforms which express dependencies between the technical parameters: capacity per hour, “Qh”, active power of the working wheel unit, “N”, specific consumption of electricity “e”, and specific resistance to cutting the marly clay formations being excavated, “kL”, and the technological parameters: the thickness of the cut piece, “S”, cutting height, “h”, and the speed of the working arm, “vk”, a nomogram is built by bringing together the origins of the regression analysis platforms based on quadratic laws. The values of the technical parameters can be easily determined in this nomogram if we start from the coordinate axes in which the variation interval of the thickness of the cut piece, “S”, is presented on the apshise and the variation of the working arm speed, “vk”, is presented on the ordinate.
Figure 8. Nomogram of the dependency of technical and technological parameters where cutting height \( h = 4 \text{ m} \). In 1\textsuperscript{st} quadrant the value of the capacity per hour \((Q_h)\) is determined, in the 2\textsuperscript{nd} quadrant the value of the active power of the working wheel \((N)\), in the 3\textsuperscript{rd} quadrant the value of the specific consumption of electricity \((e)\) and in the 4\textsuperscript{th} quadrant the values of specific resistance to cutting \((k_L)\).

**Conclusion**

We have analysed the results of our research in which we verified the capacity per hour of the bucket wheel excavator SRs1300 after an overhaul of the whole system, in which the working wheel and its driving unit were modified and replaced. In this case, the regressive and dispersive analysis with computer simulation models using first order 2\textsuperscript{k} orthogonal plans with many factors demonstrate that after overhauling the system the values obtained are favourable compared to those obtained before the overhaul when measuring the capacity of this excavator, noting that the actual geomechanic conditions of the fields of Sibofci where the tests took place were identical before and after the overhaul, most notably the specific resistance to cutting was \( k_L \approx 70[\text{daN/cm}] \). In this case we observed the capacity increased 5\%, whereas the energy parameters of power of the working wheel and specific consumption of electricity were lower by 10\%. Therefore, modification of the excavator’s working unit is justifiable, because it can increase the productivity of the excavator and lower the consumption of energy by these excavators working in surface mines in Kosova.

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Comparison of Single Curvature, Single and Double Layered Space Truss Systems Regarding Their Weights

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Abstract: Space truss systems are aesthetic and safe systems that can pass wider spans economically. In this context, space truss systems can be used in different ways. Therefore, in this study, the system weights, unit weights and midspan displacements of single curvature single and double layered (vault) space truss systems were investigated. The systems were modelled and analyzed with Finite Elements Method. “Mode Combination Method” was used for the dynamic analysis. 56 single and double layered circular, elliptical and parabolic systems with varying span lengths were solved using a computer program whose results were expressed with tables and diagrams. As a result of analyses performed by this study, the investigation of each span length prepared with different geometries (circular, elliptical and parabolic) in terms of their weights presented significant outcomes for various geometric height/span length ratios.

Key words: Space Truss System, Single Curvature, Single Layered, Double Layered, System Weight, Unit Weight, Geometry, Circle, Ellipsoid, Parabola

Introduction

Wind and snow loads are significant loadings for space truss systems especially during their design stage. Single and double curvature space truss systems are more durable against wind and snow loads in comparison to the other geometries. Therefore, the geometry of the system should be well-selected when wider spans are passed using space truss systems, since a well-selected geometrical shape will bring the most appropriate design together itself (Constantin et al., 1984).

In order to make use of space truss systems efficiently, the effects of the parameters such as system height, system geometry, module length and layout of the supports should be understood. The factors such as span length, number of nodes and bars exhibit the most appropriate structural behavior for the system which should be considered during the design stage. Single and double layered space truss systems provide the most appropriate structural behaviour (Esen 1995).

The weights and costs of the space truss systems increase with the increasing span length as for the shallow systems with lower geometrical heights. The most appropriate systems have 1/4 ratio of height/span length in terms of geometrical height. The ideal value of beam height between layers was achieved by dividing the longitudinal span length to the frequency value (Çınar, 2001). The spring or line segment shifted in space truss systems is called as vault length, and the spring or the line segment on which the vault length was shifted is called vault width (Türkçü, 2003) (Figure 1).

The objective of this study is to examine single curvature single layered (Figure 2) and single curvature double layered (Figure 3) space truss systems with circular, elliptical and parabolic cross-sections in terms of their weights. After examining the system weights, unit weights and midspan displacements of single curvature single and double layered 56 space truss systems, the static and dynamic analyses of the systems were performed with finite elements method. “Mode Combination Method” was used for the dynamic analysis, and all the obtained outcomes were expressed using diagrams.

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**Figure 1.** Vault length and vault width

Figure 2. Single curvature single layered space truss system
(a) Space truss system with circular cross-section
(b) Space truss system with elliptical cross-section
(c) Space truss system with parabolic cross-section

Figure 3. Single curvature double layered space truss system
(a) Space truss system with circular cross-section
(b) Space truss system with elliptical cross-section
(c) Space truss system with parabolic cross-section

**Loads and Materials**

**Loads**
The loadings used for system modeling were as in the following:
Dead Load \((g_1)\): Different at each nodal point, determined after static calculations.
Coating + purlin load \((g_2) = 30.0 \text{ kg/m}^2\). Coating material and purlin material were taken as aluminum trapeze and aluminum profile, respectively.
Installation load \((g_3) = 10.0 \text{ kg/m}^2\), Snow load \((P_{ko}) = 115.0 \text{ kg/m}^2\) (from Table 4 in TS498 for 2nd degree snow region)
Wind load (W) = 80.0 – 110.0 kg/m² (Table 5 in TS 498)
Temperature difference (Δt) = ± 25 °C

The systems that will be analyzed were assumed to have Z3 type soil class in 4th degree seismic zone. According to these assumptions, the values taken from the Seismic Code and used for calculations were:

- Effective gravitational acceleration coefficient: \( A_o = 0.10 \) (for 4th degree seismic zone)
- Building significance coefficient: \( I = 1.0 \)
- Spectrum characteristic periods: \( T_A = 0.15 \) and \( T_B = 0.60 \) (for Z3 type soil class)
- Behavior coefficient of load-carrying system: \( R = 5 \) (ductility level for normal systems)

**Material properties**

St 52 steel type whose material properties are given in Table 1 was selected for the systems analyzed in this study.

<table>
<thead>
<tr>
<th>Material Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unit weight (gr)</td>
<td>7.85 t/m³</td>
</tr>
<tr>
<td>Modulus of Elasticity (E)</td>
<td>21000000 t/m²</td>
</tr>
<tr>
<td>Poisson Ratio (ν)</td>
<td>0.3</td>
</tr>
<tr>
<td>Yielding point (( \sigma_f ))</td>
<td>36000 t/m²</td>
</tr>
<tr>
<td>Tensile strength (( \sigma_d ))</td>
<td>52000 t/m²</td>
</tr>
<tr>
<td>Shear Modulus (G)</td>
<td>8100000 t/m²</td>
</tr>
<tr>
<td>Thermal Expansion Coefficient (Δν)</td>
<td>0.000012</td>
</tr>
</tbody>
</table>

**Analysis and Design Results**

Single curvature single and double layered space truss systems were prepared in circular, elliptical and parabolic geometries with 30, 40, 50, 60, 70, 80, 90 and 100 m span lengths in the direction of vault length. Although the geometrical heights for elliptical and parabolic systems were 20, 25 and 30 m, they varied for circular systems. The vault width was 50 m for every type of systems. The module height and frequency were taken as 2 m and 60, respectively. There were existing 2481 nodal points, 9600 bars and 42 supports in all the systems.

**System weights of single curvature single and double layered space truss systems**

Single curvature single and double layered space truss systems have a module height of 2 m. The effects of the variations in the geometry of the vault length arch, geometrical height and vault length on the system weight were investigated. The analysis and steel design for 56 systems formed with circular, elliptical and parabolic geometries were performed. The other geometrical factors remained same for all the systems. At the end of the analyses and designs, the variations of the system weights of single curvature single and double layered space truss systems with respect to span lengths were presented in Figure 4.

As seen in Figure 4, although the number of bars in double layered systems is more than that of single layered systems, the system weights of double layered systems are lighter than those of single layered systems for the same span lengths. This is due to hinged type of nodal points constructed for double layered systems but not for single layered systems. When nodal points are hinged, the bars do not carry shear force, bending and torsion moments but only axial tensile and compressive forces. Therefore, the system weight decreases with decreasing bar cross-sections. However, it is impossible to construct hinged nodal points for single layered systems, because the system becomes labile with them. The bars are joined with special nodal point details formed by welding or using bolts. Since the construction of nodal points using hinges is not possible, besides axial tensile and compressive forces there occur bending moment, shear force and torsion moment on the bars of the system. Therefore, the bars should be checked with respect to the additional forces and moments that this will increase the cross-sections and naturally the systems weight.
Unit weights of single curvature single and double layered space truss systems

The unit weights of single curvature single and double layered space truss systems were calculated by dividing their system weight to the area covered by the system. All the unit weight variation diagrams of single curvature single and double layered space truss systems with respect to the systems’ span lengths are given in Figure 5.

As seen in Figure 5, the unit weights of double layered systems are greater than those of single layered ones for all geometries and span lengths. According to the previous studies and applications performed up to now, the most appropriate unit weight values for the space truss systems should be about 10 - 30 kg/m². As it can be clearly seen in the diagram, the unit weight values of double layered space truss systems also lies between this intervals. However, the system weights and also the unit weights of single layered space truss systems were obtained higher due to the unavailability of constructing hinged nodal points and the existence of some other forces besides axial loads acting on the bars.

While the least unit weights for 30m span lengths were obtained for single and double layered circular systems, the largest unit weights of the same span length were obtained for the elliptical systems of 30m geometrical height. The increasing span length resulted in having the largest unit weight for the circular-shaped systems. Although the single layered parabolic-shaped systems with 20 m geometrical height had larger unit weights initially, they went through a most appropriate system after achieving the span lengths greater than 40 m. Moreover, the least unit weight was obtained for double layered parabolic systems with 30 m geometrical height when the span length greater than 80 m was achieved. The unit weights of the systems decrease with the increasing span lengths. The system in circular geometry had the largest unit weight for 100 m span length. The minimum unit weights for the same span length of single and double layered systems were obtained for the parabolic system of 20 m geometrical height and for the parabolic system of 30 m geometrical height, respectively.
Figure 5. Unit weight variations of single curvature single and double layered space truss systems with respect to span lengths

**Midspan displacements of single curvature single and double layered space truss systems**

All the vertical midspan displacements determined for single and double layered space truss systems are shown in Figure 6. All the displacements were subjected to displacement check and observed to be less than the displacement limit.

Figure 6. Midspan displacement - span length diagram for single and double layered space truss systems

As seen from the diagram, the minimum displacement values were observed for double layered systems that support each other by the help of bottom flange, upper flange and diagonal bars. In this way, the system behaves more stable. Additionally, the system weight being less than that of single
layered systems is another reason for having smaller midspan displacements in double layered space truss systems.

When the span of vault length arch is 30 m, the displacement in the single and double layered systems occurs at the systems with circular cross section. The geometrical height of the circular systems increases with the increasing span length. As it is clearly seen in the diagram, this condition causes the midspan displacements of the circular cross-section systems become larger than those of the other systems.

The elliptical systems of 20 m geometrical height presented the most appropriate midspan displacement values for single and double layered space truss systems of 40 m and 90 m span lengths. Additionally, the space truss systems with circular geometries had the largest midspan displacement values after the span length greater than 70 m was achieved.

The most appropriate systems for 100 m span length in terms of displacement are the parabolic-shaped systems with 20 m geometrical height. The circular systems with the same span length presented the largest displacements again. The other space truss systems had intermediate midspan displacement values.

**Results and Conclusions**

In this study, single and double layered 56 space truss systems in circular, elliptical and parabolic geometries with different span lengths were designed, analyzed and compared to each other. They were modelled with 2 m module height. Moreover, for the same span lengths, the circular-shaped systems were modelled, designed and analyzed for 2.5 m and 3 m module heights.

When the tables and graphs prepared as a result of calculations were examined, the double layered systems provided more suitable design and more economic results when compared to the single layered systems. In double layered systems, system weight, unit weight and midspan displacements were always obtained smaller. Although the system weights of single layered systems are heavy, they are always lighter systems in comparison to the classic steel systems covering the same area.

When the measures of system weight, unit weight and displacement were considered, the most appropriate geometry for single curvature single and double layered space truss systems with span lengths greater than 40 m was parabolic-shaped geometry. Up to 60 m span lengths, elliptical-shaped systems can also be another appropriate solution. Unit weight is calculated by dividing the system weight into the area covered by the system. Since the vault width is constant, the system areas will be constant for the same span length. Therefore, the unit weight is completely dependent to the system weight. Circular geometry can be an appropriate solution up to 40 m span lengths of single and double layered systems. However, since the unit weights of the systems in circular geometry will increase with the increasing span length, parabolic and elliptical shaped systems are the most appropriate systems in terms of unit weight for the systems having more than 40 m span lengths. The unit weights of double layered space truss systems are lighter than those of single layered systems. The unit weight variations of all the systems are closer to each other. While the most unfavourable solution for a double layered system is the circular shaped system, the elliptical and parabolic shaped systems are the most appropriate ones in terms of unit weight.

When the systems were discussed in terms of their midspan displacements, single layered space truss systems presented larger displacements with respect to those of double layered systems. Double layered systems displayed a more balanced condition with their bottom flanges, top flanges and diagonal bars when compared to single layered systems. Moreover, since the weights of the single layered systems have higher values, their displacement values also increase. Increasing span length causes to have increase in midspan displacements which occurs larger for the systems in circular-shaped geometries when compared to the other geometries. The most stable systems in terms of displacement values are elliptical systems. The displacement values of parabolic systems take the intermediate values.

As a result, the construction of space truss systems with double layers is the most appropriate and exact solution that the system weight, unit weight and displacement values of double layered systems were obtained appropriately. Since the double layered space truss systems best fit the definition of space truss systems, they were mostly used in practical applications. However, single
layered space truss systems are rarely preferred due to their larger weights, difficult assembling and some additional costs. Moreover, single curvature single layered systems can not be a reliable solution for wider spans and should be used for shorter spans.

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Energy and Environment in the Balance–Kosova Case

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Abstract: The most abundant natural resource in Kosovo is lignite type coal, which was extensively used in electricity power plants and at a time in Lurgy Gasification Process. But, exploitation of lignite was done without respect to environmental capacity of the country. For example, uncontrolled burning of lignite in power plants each year left in Kosovo environment about 2,000,000 tons of fly and bottom ashes, more than 100,000 tons of sulfur, of which more than 50% is organic, over 12 tons of arsenic, about 3 tons of beryllium, 1 ton of cadmium, 351 tons of nickel, 492 tons of titanium, 191 tons of manganese, etc. This paper deals with the examinations of some parts of complex organic substance and presence of heavy metal ions in it.

Keywords: lignite, power plant, fly ash, bottom ash.

Introduction

In recent years, both the scientist and ordinary people have become increasingly aware of the problems of energy. Coal as fossil fuel is the most abundant fossil fuel resource in most countries including Kosovo, and many studies described it as the bridge to future energy systems, while stressing world coal prospects, environmental problems, resources and energy projections (World Energy: Looking ahead to 2020).

A report by the World Coal Study (1980) stressed that coal will have to supply between one-half and two-thirds of the additional energy needed by the world and that to achieve this goal world coal production will have to increase 2.5 to 3 times, and the world trade in steam coal will have to grow 10 to 15 times above the 1979 levels (Kargey, 1983). Those projections are based on the World Natural Resources (Energy Reserves) which shows that Coal comprise 61% of world energy reserves; oil 15%, natural gas 15% and oil shale 9% (Charles, 2005).

Coal is the main National Natural Resource of Kosovo (containing about 50% of Resource value) and has attracted scientific interest of many researches and studies, including deposits, chemical composition and structure as mush as environmental problems and solutions (Daci, 1981, 1983, 1984, 1985, 1996).

Coal potential as an alternative energy source is going to depend on how well its environmental problems are understood and then solved.

Energy and Environment are essential for sustainable development. Sustainable development is the term for the dual imperative – economic growth and environmental sustainability that has been gaining ground among business leaders since the 1992 United Nations Earth Summit in Rio de Janeiro (Magrella, 2000).

Energy is central sustainable development and poverty reduction efforts. It affects all aspects of development – social, economic and environmental – including livelihoods, health, population levels, education, etc. None of the Millennium Development Goals can be met without major improvement in the quality and quantity of energy services in developing countries (UNDP, 2007).

Lignite type coal in Kosovo was extensively used in electricity power plants and at a time in Lurgy Gasification Process. Unfortunately the exploitation of lignite was done without respect to environmental capacity of the country and almost has created an environmental bomb for population. For example, uncontrolled burning of lignite in power plants each year left in Kosovo environment about 2 million tons of fly and bottom ashes, more than 100,000 t of sulfur, of which more than 50% organic, over 12 t of arsenic, about 3 t of beryllium, 1 t of cadmium, 351 t of nickel, 492 t of titanium, 191 t of manganese, etc.

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Coal is composed of mixtures of organic compounds of carbon, hydrogen, oxygen, nitrogen, sulfur, etc. along with some inorganic matter which is identified in the residual ash after combustion. The organic matter is largely composed of polycyclic aromatic structures and in addition to carbon and hydrogen contains significant quantities of organic oxygen (as methoxy, hydroxy, carbonyl and carboxyl), nitrogen and organically bound metals. Many metal or metalloid elements that might be expected to form some types of organometallic compounds or stable organic complexes are relatively high levels in coals.

**Results and Discussion**

The fact that coal contains many potentially toxic trace elements like As, Be, Cd, Hg and Pb, together with the fact that most of mined coal in Kosovo is burned to generate electric power, has led to a great deal of interest in the trace element contents of this coal. The results that were achieved in determining chemical composition of ashes from Kosovo coal are shown in Table 1.

<table>
<thead>
<tr>
<th>Constituents</th>
<th>Percentage of compounds</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>20.75 – 27.20</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>4.00 – 8.23</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>4.94 – 10.77</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.42 – 0.50</td>
</tr>
<tr>
<td>CaO</td>
<td>46.03 – 40.98</td>
</tr>
<tr>
<td>MgO</td>
<td>4.01 – 4.40</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>0.67 – 1.16</td>
</tr>
<tr>
<td>SO₃</td>
<td>7.94 – 13.74</td>
</tr>
<tr>
<td>Na₂O</td>
<td>1.29 – 1.56</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.16 – 0.18</td>
</tr>
<tr>
<td>MnO</td>
<td>0.17 – 0.21</td>
</tr>
</tbody>
</table>

Whereas some of the overall chemical characteristics of studied coal samples are shown as follows. Moisture 26.83%, ash 26.58%, $S_{\text{total}}$ 1.61%, $S_{\text{pyrinite}}$ 0.53%, $S_{\text{org}}$ 0.95%, OCOOH 25.73%,

![Kosovo lignite reserves compared to the world](http://wikimedia.org/wikipedia/en/b/b4/Kosovo-lignite.jpg)
O_H 26.91%, O_ether 35.89%. In order to get more information’s about the chemical structure of organic substance and trace metals organically bound, we used two types of solvents for extractions, dioxane as aprotic and cyclohexanole as protic solvent.

In the case of dioxane extraction the yield of extract was 26.50 wt%. The extract was fractionated in its acid / base / neutral components (figure 1). After a wet ashing procedure a set of elements including: K, Ca, Mg, Fe, Pb, Zn, Cu, Mn, Cr, Cd, Co and Ni were analyzed by AAS. Seven other elements including Ba, Sr, Be, B, Al, Ga and V were analyzed by Inductively Coupled Plasma – Optical Emission Spectroscopy (ICP-OES).

Obtained results for separation of dioxane extract in its acidic, base and neutral components are presented in Figure 2.

**Figure 2.** Acids, phenols, bases, neutrals separation scheme
Figure 3. Fractionation scheme for cyclohexanol extract

Separation of dioxane extract in its acid, base, neutral components, benzene insoluble and petrol ether insoluble fractions, gave us a chance to get more detailed picture of presence of trace metals in different kinds of organic compounds present in Kosovo coal. Obtained results are shown in Table 3.

In case of cyclohexanol extract, we also used the same methodology as extraction technique and separation of extract in its acid/base/neutral and Bi as well as Pi insoluble fractions. The decomposition of the extract (19.98 wt%) and its fractions was affected by wet ashing (acid dissolution HClO₄-HNO₃) to prevent the loss of potentially volatile elements that are part of coal substance.

In the extract and its fractions, the concentrations of K, Ca, Mg, Fe, Pb, Zn, Cu, Mn, Cr, Cd, and Ni were determined by AAS, whereas concentrations of Al, Ba, Sr, Be, Ga, and V were monitored via Inductively Coupled Plasma – Optical Emission Spectroscopy.

The concentrations of analyzed trace metals in cyclohexanol extract and its acid/base/neutral components and Bi as well as Pi fractions are shown in Table 4.
Table 3. Metal analysis data for acid/base/neutral, Bi (benzene insoluble) and Pi (petrol ether insoluble) fractions of dioxane extract.

<table>
<thead>
<tr>
<th>Fractions (Micrograms/gram substance)</th>
<th>Acids</th>
<th>K</th>
<th>Ca</th>
<th>Mg</th>
<th>Fe</th>
<th>Pb</th>
<th>Al</th>
<th>Ba</th>
<th>B</th>
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<td></td>
</tr>
<tr>
<td>Amines</td>
<td></td>
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<td></td>
</tr>
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<td>Neutrals</td>
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<tr>
<td>Bi</td>
<td></td>
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<tr>
<td>Pi</td>
<td></td>
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Table 4. Metal concentrations (μg/g) in cyclohexanol extract and its fractions

<table>
<thead>
<tr>
<th>Fraction</th>
<th>Extract</th>
<th>Acidic</th>
<th>Phenolic</th>
<th>Amine</th>
<th>Neutral</th>
<th>Bi</th>
<th>Pi</th>
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<td>6876</td>
<td>1406</td>
<td>2129</td>
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<tr>
<td></td>
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<tr>
<td></td>
<td>Cr</td>
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<td>340</td>
<td>146</td>
<td>988</td>
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<td></td>
<td>Cd</td>
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<td>Ni</td>
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<td>Ga</td>
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<td>749</td>
<td>216</td>
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<td>V</td>
<td>6</td>
<td>59</td>
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</table>

Conclusions

On the bases of obtained analytical values for concentrations of analyzed trace elements in different classes of organic compounds in dioxane and cyclohexanole extracts, the following conclusion remarks can be drawn:
a) Very high content of oxygen functionalities in form of carboxyl and hydroxyl oxygen in Kosovo lignite type of coal permits the ionic bonding of trace elements investigated in the acidic and phenolic fractions of both extracts. The highest levels of concentrations of elements that prefer oxygen-like bonding were Fe, Al, B, Zn, Al, Ca, Mg, Sr, Pb, Ga and V.

b) Some of the elements investigated in extracts and their acidic/basic/neutral components are predominantly coordinative bonded with nitrogen, and high concentrations were found in the amine fraction. Among these elements are: K, Al, Ni, Ga, Cu.

c) There is no doubt that the analyzed metals are associated with the heteroatom (O and N). It may therefore be suspected that many metals in the coal extracts that were studied exists as carboxylates and phenolates, implying the ionic bond character of these linkages. The metals that are associated with nitrogen in base fractions probably exist as metal chelates.

References
Seismotectonic Settings and Seismicity of Kosovo

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Abstract: In this scientific work presented are basic characteristics of the seismicity of Kosovo, for the period 1901 to 2008 with emphasis on the most active regions. Compilation and updating of earthquake data was made in order to define an earthquake catalogue for territory of Kosovo, which will provide a basis for determination of the main characteristics of the seismicity of Kosovo. Results of the existing investigations were a basis for defining the regional geologic, seismologic, neotectonic and seismotectonic characteristics of the area as well as definition of seismogenic sources. These investigations have great significance from scientific and applied aspect and will provide reliable assessment of Kosovo seismicity. Results can be used as input for further investigations in the field of seismic hazard and risk assessment and engineering seismology as well for physical and urban land use planning and design in seismic prone areas.

Keywords: Kosovo, seismotectonics, seismic hazard

Introduction

The territory of Kosovo is active from the seismic point of view. The evidences for the earthquakes of the past testify this. In this regard we can mention the earthquake of Prizren, occurred on 1456 year, with epicentral intensity VIII degree of the MSK-64 scale and magnitude MS=6.0 (Sulstarova et al., 2005), the earthquake of Pejë occurred on 1662 year, with intensity of VIII degree of the MSK-64 scale and magnitude MS=6.0 (Sulstarova et al., 2005). In the more recent period of time, we have in Kosovo the earthquake of 1921 year in Ferizaj region, with intensity of IX degree of the MSK-64 scale and magnitude MS=6.1 (Sulstarova et al., 2005), the earthquake of the year 1980 that hit the Kopaonik region, with intensity VIII degree of the MSK-64 scale and magnitude MW=5.9 (CMT), and finally the earthquake of the year 2002 with epicentral intensity VIII-IX degree of the MSK-64 scale and magnitude MW=5.7 (CMT) that heavily hit the Gjilan Municipality (Elezaj, 2002). On the same time, it should be mentioned that the territory of Kosovo has been affected several times with severe destructions caused by the earthquakes occurred in the neighbouring countries, like Albania, Montenegro, Macedonia, Serbia, etc.

Thus, based on the latest achievement in this field, it is necessary the analysis of seismic hazard of the Kosovo territory to be undertaken, in order to have a realistic evaluation of this phenomena and to contribute for the mitigation of earthquake consequences. In practise, the seismic hazard analysis consists on the evaluation of the failure potential of the earthquake phenomena that could happen in a certain region during a certain period of time. Earthquakes strike without warning and in this context, the best preparation would be the improvement of the structures design, in order to make them more resistant against the seismic action. The seismic hazard assessment is a very important aspect in the framework of the continuous efforts for the mitigation of the earthquake consequences in every country. The simplest examples of a seismic hazard assessment are the maps of the historical earthquakes that have occurred in a certain region. Although very useful, these maps are insufficient for the characterization of seismic action in terms of ground motion parameters.

Certainly, after more than two decades, many changes have occurred regarding the theoretical and methodological aspects of seismic hazard assessment, as well as the database is concerned, which has been enlarged in the last years, thanks to the technological developments and consistency of the monitoring networks in all the countries of the region. Developed countries update their seismic hazard maps, as a rule every 5-10 years. The new generation of the seismic hazard maps are based entirely on the
probabilistic methodologies, which consist on the quantitative assessment of ground motion in a given site resulting from an earthquake that can occurs within a specified interval of time. In more concrete terms, the seismic hazard on a given site is defined as the expected value of any ground motion parameter (acceleration, velocity, spectral ordinates, macroseismic intensity, etc.), that with a given probability is not exceeded within a certain period of time. Usually, the seismic hazard assessment programs specify 10% exceedance probability of some threshold of any ground motion parameter, for 50 years of exposure, which corresponds to the 475-year return period. For critical and other important structures it is absolutely necessary that higher standard levels be applied, dependent of the human and material consequences that may derive from their destruction.

Seismic hazard maps are an important tool for the urban planning, evaluation and mitigation of consequences of the future earthquakes as well as for the necessary countermeasures planning in order to withstand human and material losses, etc. These maps are today on the base of the seismic design codes and nowadays design standards, which in case of earthquakes, aims to: a) protect the human life; b) limit the damages; c) the important structures of civil protection to remain functional. The random nature of the seismic events and the limited resources available, to counter their effects are such as to make the attainment of these goals only partially possible and only measurable in probabilistic terms (Eurocode 8, EN 1998-1:2004).

The present study is result of many years of authors experience in the field of seismic hazard assessment, expressed through the publication of a large number of papers and presentations in journals and international conferences. Considering the rapid progress of the methodology and practice of seismic hazard assessment, we believe this study will serve as a good base for the microzonation studies to be followed in the municipalities and towns of Kosovo, as well as for the improvement of the structure design practice. The establishment of the Seismological Institute of Kosovo, as well as the beginning of the seismic activity monitoring of the country, is a great achievement in this regard that will enrich the information for the earthquake phenomena on the territory of Kosovo and will enable the further refinement of such kind of studies in the future.

The Seismotectonic Framework and The Seismicity of Kosovo

On the worldwide seismic zonation, Kosovo takes place on Alpin-Mediterranean seismic belt. This belt comprises the wide zone of contact between lithospheric plates of Africa and Eurasia, from Azores Islands up to the eastern border of Mediterranean basin. In this zone, the concept of plate tectonics is especially complicated from the presence of numerous blocks and the release of stress through plastic deformation on a large part of the zone.

Geological contents and morphological characteristics of the Kosovo territory are very complex, with a lot of morphological contrasts, with many mountains over 2,500 meters, and in the same time, with large depressions. During the recent geological period the region has been embraced from the neotectonic processes which have conditioned the formation of many structural units that are expressed by intensive uplifting and sinking movements. The territory of Kosovo with these prevailing movements’ tendencies is divided by a large number of blocks along the faults. A large number of these tectonic faults represent seismogenic alignments that often are not active along their entire length due to the interception with other transverse faults.

Neotectonics structure of Kosovo

Neotectonic, as is known, studies on new structures, their coverage on the relief of Earth's surface and different types of tectonic movements and the dynamic processes that condition them. It studies how new movements of tectonic movements as well as today, affecting the Earth's crust affect. Aspects of Neotectonic research in territory of Kosovo are closely related with studies of morph-structure units borne from the neotectonic movements, at times on the new geological, during Pliocenic and Quaternary, in the so-called neotectonic stage.

Study Kosovo’s neotectonic activity is closely related to the early recognition of geological structure, to detect relation between early tectonic movements and neotectonic movements. During neotectonic stage, territory of Kosovo is included by tectonic processes, which have conditioned the formation of new morph-structure’s units: morph-structure with dominant tendency on rising trend and dipping.
Structures with morph structure tendency on the rise and characterized by trends in diving

Lands with dominant tendencies on the rise, on the neotectonic map should be limited with deformation neotectonic isoline, which show the real value of vertical rise during Neogen and Quaternary. In current days, past-volcanic are manifested with water thermo-minerals water phenomenon, which testifies to the existence of expressed geothermal field. Lands of Kosovo with dominant rising trend we have divided into separate units, appointed with numbers from 1 to 13, Uplifting units (Figure 1; Elezaj, 2002):

Figure 1. Uplifting units

Figure 2. Depression units
In the territory of Kosovo are very much expressed the neotectonic units, which represent morphostructure dipping. These are large lowlands known as Neogen, which are accumulated in large measure of terigen molasic material, where are also found large reserves of coal. Are known these lowlands (see Figure 2) (Elezaj, 2002):
- Lowland of Kosovo
- Lowland of Dukagjin,
- Lowland of Drenica
- Lowland of Podujeva
- Lowland of Krivareka

**Figure 3. Seismotectonic map**

**Seismotectonic characteristics**

During the evaluation of seismic activity, based on existing data experience from research carried out, can be seismotectonic Kosovo in detail how the data provided by seismological statistics.

Structures with morph structure tendency on the rise,
Structures of characterized by trends in diving,
Volcanic complexes, Earthquake epicentres
Disjunction structures; disjunction expressed by contrast field, disjunction expressed weak field disjunction of imagining, old dissociation, Seismotectonic map Figure 3. (Sh. Mustafa)
Probabilistic Seismic Hazard Assessment of Kosovo

The methodology of seismic hazard assessment

In the process of assessment of seismic hazard through probabilistic methods, the main difficulties that one can encounter are two:

- Earthquake catalogue completeness
- The need to specify seismic source zones

In Figure 4, presented is the earthquake epicentre map for the region [18-24°E, 38-44.4°], based on the catalogue compiled for the needs of this project (LlambroDuno, Neki Kuka, Shemsi Mystafa), comprising 2500 years period of time starting from 510 B.C up to 31/12/2008. The earthquake size is expressed in terms of moment magnitude, $M_W$.

![Figure 4. Distribution of the earthquake epicenters in the study region (period 510 B.C. – 31/12/2008, MW≥4.0)](image)

2.2 Assessment of seismic activity

For the assessment of seismic activity we choose as recurrence model the double truncated exponential approach. The maximum likelihood method was chosen for the assessment of recurrence parameters, as it is described in Bollinger et al., (1993), Weichert (1980) and Berril and Davis (1980). This method is considered the most appropriate compared to least square one for the assessment of recurrence parameters, because utilizes all the available data and weighting then according the observational intervals of the earthquake catalogue completeness.

Another method for the assessment of recurrence parameters is that proposed by Kijko and Selevoll (Kijko and Selevoll, 2004). Except the instrumental data, this approach considers the earthquake macroseismic information gathered during the course of the history, as well. The mean annual rate of seismic activity $\lambda$, $b$ parameter of the G-R relation, as well as the regional maximum magnitude $M_{\text{max}}$ are evaluated through the maximum likelihood approach, using the Bayesian formalism.

The above mentioned parameters ($a$, $b$, $\lambda$, $M_{\text{max}}$) were globally evaluated for the square [19.5-22E, 41.5-43.5N] that includes Kosovo, as well as for the region [18-24E, 40.5-44.4N] that includes Kosovo and about 150 km from its border. Further, these parameters were evaluated according the
identified zones distinguished from the spatial earthquake distribution. Each of these zones is characterized by a specific frequency-magnitude relationship derived by the historical data (macroseismic intensities) as well as instrumental ones. The zone delineation has been performed taking into account the similarity of the geodynamic behaviour as well as the homogeneity of the spatial earthquake epicentre distribution. The assessment was performed using two methods: the maximum likelihood approach (Bolinger et al., 1993), and the Bayesian formalism through the parametric-historic procedure of Kijko-Selevoll (2004).

Table 1. Recurrence parameters, assessed according Bollinger et al., (1993) and Kijko-Selevoll (2004)

<table>
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<tr>
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<th></th>
<th></th>
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</thead>
<tbody>
<tr>
<td></td>
<td>Mmax</td>
<td>a-value</td>
<td>b-value</td>
<td>λ (M≥4.5)</td>
</tr>
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<td>A0</td>
<td>43.6.0</td>
<td>7.129±0.465 1.628±0.098</td>
<td>0.633±0.086 1.920±0.26</td>
<td>0.590±0.09 6.06±0.12</td>
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<tr>
<td>A1</td>
<td>57.7.2</td>
<td>3.889±0.096 0.918±0.018</td>
<td>0.575±0.048 0.900±0.10</td>
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<td>A2</td>
<td>77.6.8</td>
<td>4.599±0.133 1.031±0.026</td>
<td>0.913±0.060 1.070±0.09</td>
<td>0.770±0.10 6.85±0.11</td>
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<tr>
<td>A3</td>
<td>247.7.0</td>
<td>5.592±0.284 1.133±0.057</td>
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<td>60.5.7</td>
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<td>37.6.1</td>
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<td>45.5.9</td>
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<td>0.571±0.067 1.230±0.27</td>
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<td>24.6.5</td>
<td>4.052±0.236 1.021±0.046</td>
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<td>85.7.7</td>
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<td>6.101±0.490 1.333±0.098</td>
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<td>5.447±0.248 1.119±0.048</td>
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</tr>
<tr>
<td>18-24E</td>
<td>40.5-44.4N</td>
<td>628.7.7       6.405±0.073 1.223±0.015</td>
<td>7.942±0.066 1.28±0.03</td>
<td>7.45±.31 7.90±28</td>
</tr>
</tbody>
</table>

In both cases, the data have been weighted appropriately taking into account the completeness periods according the magnitude threshold mentioned above. The results taken by the two methods (Table 1) are comparable and any remarkable difference is not observed. The mean results taken by the two methods were used by us into the calculations of seismic hazard.

For the b parameter we accepted the value b=1.25, whereas the maximum magnitude for the region that includes the Kosovo territory is accepted the value Mmax=6.8. The recurrence model for the region [19.5-22E, 41.5-43.5N] is shown in the Figure 5. This is a double truncated exponential model, with b=1.25, Mmin=4.5 and Mmax=6.8. As it can bee seen, the consistency between the model as well as the observed data is very good, that gives a satisfactory level of credibility to the earthquake recurrence law.
Employing the parametric-historic procedure of Kijko-Selevoll (2004), the hazard curves in terms of magnitude (the accidence probabilities of specified values of magnitude) for the region [19.5-22E, 41.5-43.5N] were computed. The results are presented in the Table 2.

It is seen from the Table 4, that the recurrence period for the earthquakes with magnitude $M_W=5.0, 5.5, 6.0$ and $6.5$ are $3.1, 14.2, 69.8$ and $502.4$ years, respectively; while an earthquake with $M_W=6.7$ is replicated in average every 2446 years. From the probabilistic point of view, every year in Kosovo an earthquake with magnitude until $5.0$ with probability 27.8% is expected; every 50 years an earthquake with $M_W=6.0$ with probability 51.2% is expected; and every century is expected an earthquake with magnitude up to 6.0 with probability 76.2%.

2.3 Results of seismic hazard assessment

The result of the seismic hazard analysis is the assessment of the probability that a certain ground motion parameter (PGA, SA, PGV, etc.) can be exceeded in a given period of time. In order the maps compiled to be compatible with the nowadays aseismic design standards, we calculated the seismic hazard for the entire Kosovo territory for different safety levels (LlambroDuno, Neki Kuka, Shemsi Mystafa). So, the assessment were performed for: 10% exceedance probability in 10 years, that corresponds to the return period $RP=95$ years; 10% exceedance probability in 50 years ($RP=475$ years); 5% exceedance probability in 50 years ($RP=975$ years); 2% exceedance probability in 50 years ($RP=2475$ years); 1% exceedance probability in 50 years ($RP=5000$ years) and 1% exceedance probability in 100 years ($RP=10000$). The objectives of the study were the maximum horizontal components for PGA and spectral accelerations $SA_{10, 5, 3.3, 2, 1}$ and $0.5$ Hz.

For the assessment of the above mentioned ground motion parameters, the Bindi et al. (2009), Berge-Thierry et al., (2003), and Boore and Atkinson (2008) equations were used. Assessment were performed for rock conditions, with velocity of shear waves $V_s=760$ m/s for the first 30 m of soil section, that corresponds Class A according the Eurocode 8 soil classification.

Seismic hazard was assessed in the grid with dimensions $0.05°x0.05°$ longitude and latitude (about $5.5$ x $4.5$ km), for an total number of 9800 nodes, which cover the entire study region (18.0°-24.0°E, 40.5°-44.4°N). First, the seismic activity index in every cell, that means the number of earthquakes with magnitude equal or larger than the lower magnitude bound $M=4.5$, was calculated. Then, the Gaussian smoothing with radius 20 km and the elliptical smoothing oriented according the main tectonic faults orientation in the region was applied into the calculated seismic activity. The double truncated exponential model was used for the modelling of the frequency-magnitude relation, with $b=1.25$, lower bound $M_W=4.5$, and upper bound that varies accordig the seismotectonic zones evidenced in the region (Table 1, last column), from 6 to 7.8.
Table 2. The recurrence intervals for different magnitude values for the Kosovo territory

<table>
<thead>
<tr>
<th>$M_w$</th>
<th>$\lambda_m$</th>
<th>Recurrence Periods (years) ± standard deviation</th>
<th>Exceedance probability</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$T=1$  $T=50$  $T=100$  $T=1000$</td>
<td></td>
</tr>
<tr>
<td>4.5</td>
<td>0.147E+01</td>
<td>0.7  0.6  0.8</td>
<td>0.769569  1.000000  1.000000  1.000000</td>
</tr>
<tr>
<td>4.7</td>
<td>0.810E+00</td>
<td>1.2  1.1  1.4</td>
<td>0.555162  1.000000  1.000000  1.000000</td>
</tr>
<tr>
<td>4.8</td>
<td>0.598E+00</td>
<td>1.7  1.5  1.8</td>
<td>0.450085  1.000000  1.000000  1.000000</td>
</tr>
<tr>
<td>5.0</td>
<td>0.326E+00</td>
<td>3.1  2.8  3.4</td>
<td>0.277931  1.000000  1.000000  1.000000</td>
</tr>
<tr>
<td>5.1</td>
<td>0.240E+00</td>
<td>4.2  3.8  4.6</td>
<td>0.213496  0.999994  1.000000  1.000000</td>
</tr>
<tr>
<td>5.2</td>
<td>0.177E+00</td>
<td>5.6  5.2  6.2</td>
<td>0.162232  0.999857  1.000000  1.000000</td>
</tr>
<tr>
<td>5.3</td>
<td>0.130E+00</td>
<td>7.7  7.0  8.5</td>
<td>0.122231  0.998524  0.999998  1.000000</td>
</tr>
<tr>
<td>5.4</td>
<td>0.959E-01</td>
<td>10.4  9.5  11.5</td>
<td>0.091460  0.991736  0.999998  1.000000</td>
</tr>
<tr>
<td>5.5</td>
<td>0.705E-01</td>
<td>14.2  13.0  15.6</td>
<td>0.068038  0.970494  0.999129  1.000000</td>
</tr>
<tr>
<td>5.6</td>
<td>0.517E-01</td>
<td>19.4  17.7  21.3</td>
<td>0.050350  0.924460  0.994294  1.000000</td>
</tr>
<tr>
<td>5.7</td>
<td>0.378E-01</td>
<td>26.5  24.2  29.2</td>
<td>0.037069  0.848725  0.977116  1.000000</td>
</tr>
<tr>
<td>5.8</td>
<td>0.275E-01</td>
<td>36.3  33.3  40.1</td>
<td>0.027138  0.747331  0.936158  1.000000</td>
</tr>
<tr>
<td>5.9</td>
<td>0.199E-01</td>
<td>50.2  45.9  55.3</td>
<td>0.019737  0.630916  0.863777  1.000000</td>
</tr>
<tr>
<td>6.0</td>
<td>0.143E-01</td>
<td>69.8  63.8  76.9</td>
<td>0.014234  0.511692  0.761555  0.999999</td>
</tr>
<tr>
<td>6.1</td>
<td>0.102E-01</td>
<td>98.0  89.7  108.1</td>
<td>0.010149  0.399521  0.639426  0.999963</td>
</tr>
<tr>
<td>6.2</td>
<td>0.715E-02</td>
<td>139.9  128.0  154.3</td>
<td>0.007120  0.300423  0.510592  0.999212</td>
</tr>
<tr>
<td>6.3</td>
<td>0.489E-02</td>
<td>204.5  187.2  225.5</td>
<td>0.004877  0.216860  0.386692  0.992470</td>
</tr>
<tr>
<td>6.4</td>
<td>0.322E-02</td>
<td>310.4  284.0  342.2</td>
<td>0.003217  0.148787  0.275436  0.960119</td>
</tr>
<tr>
<td>6.5</td>
<td>0.199E-02</td>
<td>502.4  459.7  553.9</td>
<td>0.001988  0.094728  0.180483  0.863360</td>
</tr>
<tr>
<td>6.6</td>
<td>0.108E-02</td>
<td>925.3  846.6  1020.1</td>
<td>0.001080  0.052603  0.102439  0.660656</td>
</tr>
<tr>
<td>6.7</td>
<td>0.409E-03</td>
<td>2446.4  2238.4  2696.9</td>
<td>0.000409  0.020231  0.040053  0.335532</td>
</tr>
</tbody>
</table>

Figure 6. Probabilistic seismic hazard map of Kosovo for PGA with return period 475 years, for rock conditions (Vs30 = 760 m/s). (LlambroDuno, Neki Kuka, Shemsi Mystafa)
Based on the results taken according the above mentioned procedure, the seismic hazard probabilistic maps that characterize the spatial variability of maximum acceleration Peak ground acceleration, (PGA). For every above mentioned parameters the assessment were performed for return period 475, years, that corresponds to the exceedance probabilities, 10%, in 50 year, (Figure 6).

**Acknowledgement:** The scientific work that I am presenting is the result of my activities in the geological field and seismic studies of Kosovo within several years. My studies about the seismicity of Kosovo as a seismologist - Head of Seismic Network of Kosovo in the Seismological Institute of Kosovo and as a student of doctoral studies at the University "Ss. Cyril and Methodius", Skopje, Republic of Macedonia.

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Sliding as Hillside Phenomenon in the North Eastern Part of Kosova

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Abstract: In the complex of the side phenomena of the north eastern part of Kosova, sliding who appear in a quite different dimensions play an important role in the landscape modeling; in some territories are ran in into a strong collapse, especially during tectonic abruptness. Quite developed sliding show during the tectonic contacts of magma rocks with those Terrigene, thus during the destruction streak including scrapped colluviums- proluvial materials and those diluvia of the scab conveyance. The widest expansions of these phenomena are along the limitative banks of Llapi and Kosova hollows including the hilly-mountainous and mountainous in the periphery. The laky Pliocene argil supersaturating with water during their contact with dibasic rocks but also those Terrigene flysch and regressive erosion of the Llap River branches have created conditions for displacement of scrappy material quantities set up on these argil.

Key Words: Sliding, Displacement Hillsides, Pliocene lake argil, Regressive erosion.

Introduction

The development of a spatial landscape is a multi dimensional process and it is expressed by indicators that have complex subordination between internal powers and external geomorphological agenca. General studies of the landscape of a space enables recognition of one the most complex components of a natural environment. One of natural physical–geographical units of the Kosovo space, its North Eastern (NE) part takes on an important place with characteristic features.

Natural boundaries of this space are the median valley of the river Ibër, from Mitrovica to the outlet of Bistrica river (the right anabranch) in the north west (NW), the Çyçavica mainly hilly ridge in South East (SE), the Graçanica river valley and the upper valley of Ballaban river in South East and East while all other North Eastern and north part to the peak of Pançiç (2017m) passes along the border line of Serbia-Montenegro.

It has a typical expansion North West–South East in a length of 77 km and width of 12-40 km, while the highest altitude has the bottom at Pançiç peak, one of the highest in Kosovo. The main morphological units of this part are the ridges of Kopaonik in North-West, the Greben pond of Llap in North East, North-Western part of Kosovo field in South West and hilly-mountainous side of Gollak in South East.

Taking into account the fact that the majority part of the territory of Kosovo has relatively been less studied in terms of morphological aspect; due to this reason, this work focuses on efforts for a partial approach with regard to the process of recent modeling of the landscape-sliding as hillside phenomenon quite extended in this part of Kosovo.

Sliding - Hillside Phenomenon Quite Extended

Sliding of different dimensions play an important role of landscape modeling in the complex of hillside phenomenon, which, in some territories are followed by strong collapse especially during tectonic abruptness. Relatively developed sliding are during tectonic contacts of magma rocks with those terrigene, along the streak of destructions, including mainly the koluvio-prolusion material scraps and those diluvia of the scab conveyance.

These collected materials close to abruptness detachments/separation and those complex during their morphhtectonic and morphclima tic are characterized by an instability situation, brought by considerable watercourse thanks to the level of their impenetrability. The most expansion of these phenomena is along the limitative banks of the graben pond of Llap, especially in the complex abruptness of the western bank between Pakashtica in the north and Llapashtica in the south.

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The super satiation with lake Pliocene argil water during their contact with dibasic and regressive erosion of the anabranch river Llap have created conditions for displacement of masses of scrappy materials set up on these argil. Dimension and level of development of the sliding is presented quite differently since the sliding plan in this sector gets by the contact of dibasic over tectonics rocks with Pliocene argil (Bulliqi 2000).

Thus, all under part of complex abruptness in the height of 700-900 m differs for some active sliding as such as those along the river of Pakashtica, Dobratinit, Obrançës, and Llapashtica etc. Sliding has also relatively dense expansion along the eastern pond of the Llap bank which also differs for the high level of the tectonization of the magma rocks and those flysck and molas mio-pliocen following tectonic detachment of Merdar.

Consequence of this tectonic phenomenon is the formation of a broad line of destruction during which a considerable sliding have been developed, which is expressed in the over fragmental forms of complex abruptness of an area over degraded especially between Shakovica in the south and the mouth of Merdar in the north. In a relatively smaller dimensions, the sliding meet also in the southern bank of this pond between the outlet of Batllava river and the one of Ternava which are associated/linked with setting up of lake conglomerates between Dyz and Ternava on the scab conveyance of crate of flysck (Figure 1).

Figure 1. Sliding on the left side of Batllava – Bellopojë valley (Photo Sh. Bulliqi, 2006)

The last one, being satiated with water by the conglomeratic mass water holder, which is brought by the regressive erosion of the above mentioned streams, leads to instable situation of the last ones and their continuous displacement. These bank phenomena do also have a broad expansion along the South-West bank of ridges of Kopaonik, especially from Mitrovica to the Bistrica river outlet.

In this sector, the complex abruptness is characterized by a strong tectonization of carbonated rocks which build the majority part of this abruptness thanks to the enormous amplitude of the tectonic rising of the structure of these rocks (Bulliqi 2006).

In such conditions, the developed sliding along the lines of destruction are composed of blocks and stone scraps mixed with scads of argil of the conveyance of scabs of magma rocks in most of cases. One can notice among them that sliding of the left bank of the valley of the river Dreni, Tvêrdani, Leposaviq, Bistrica, Stari Tërg etc, which are presented as active even presently, by jeopardizing residential centre and agricultural lands in fragmental forms set up on the structural levels.

Furthermore, in the sector between Mitrovica and sidelong mouth of Lebana, sliding have a considerable development especially under part of this abruptness composed of lake depositions followed by combination of gravel, sand, and argil. He lasts ones, being satiated with water from the first ones create in stabile situation for gravel and sand. In such conditions, they are replaced
continuously, urged also by regressive erosion of the river of Prodani, Tërstena, Studime, Dumnica etc by jeopardizing dwellings in the NE part of Field of Kosovo in this sector.

Figure 2. Sliding in the right bank of Ballabani valley (Photo Sh. Bulliqi, 2006)

Almost the same conditions for formation of sliding meet also in the complex of abruptness of SW bank of Gollak between sidelong mouth of Lebana and the one of Figure). Here, the sliding covers entirely terrigenous flysck rocks and those molasik of the Field of Kosovo, which are also urged by regressive erosion of the river of Besi, Siçevë, Prishtina and Graçanica.

In the upper part of these streams, sliding is developed in the dimension of flysck, which are characterized by the combination of the penetrable sand packages with the ones of impenetrable argil. Whereas, in the lower flowing, sliding is bound/linked with the combination of sands, and gravels with Pliocene lake argil.

Conclusion

- In the complex of bank phenomenon, sliding of quite different dimensions play an important role on landscape modeling of this territory, which are followed by strong sliding in some territories especially during tectonic abruptness.
- They do come across during the tectonic contacts of magmatic rocks with those terrigenous ones, Pliocene lake argil with dibasic and magmatic rocks and flysck with molase mio-pliocen. All these contacts have conditioned displacement of the masses and scrappy materials.
- They do have larger expansion on the limitative banks of the grabenor pond of Llap, especially on the complex abruptness of the western bank between Pakashtica in the north and Llapashtica in the south, then along the eastern bank of Llap pond and SE bank of the Kopaonik ridges.

References

Sheep Milk for Production Cheese Kačkaval in Kosovo

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Abstract: Milk is perfect food-SAMPURNA AHAAR. Sheep have been milked since before civilization as we know it today when nomads roamed the hills and valleys and needed the animals, meat, wool, and milk products for survival. Sheep and goats were the ideal species to provide staple diet for millions on land than could not support dairy cows. Cheese has been made for thousands of years from sheep's milk. Cheese maker can make twice as much cheese from a pound of sheep’s milk as they can from a pound of cow’s milk, but the sheep’s milk costs about four times as much. Milk processing in Kačkaval cheese takes very important place in productivity of dairy, in the same time takes very important roll in domestic economy as well as nutritive for humankind. This study is done to research the technology for production of Kačkaval cheese. This types of cheese is classified to hard group of cheeses) with a little milk to produce 1kg cheese (Until before needed need 10 litters of milk to produce 1 kg. of this kind of cheese, and now we needed 8 litters of milk to produce this kind of cheese with sheep fresh unpasteurized milk), after research and analyses of physical-chemical peculiar feature of milk, research of technological process to forming the coagulum, curd forming, storage, preparation for drying of curd and additives that we need for this technologic process of production line. We have followed the processes from drying of cheese until preparing it for market, physical-chemicals peculiar feature daily fresh cheese, 15 to 30 days maturing. Oregano - peptic peculiar feature, its storage in suitable temperatures. There were102-s of analyses to searching better production method. In fact, the best area to produce Kačkaval cheese is milk industry in Kosovo. Peculiar future of organic tasting (organoleptic) for estimation of cheese Kačkaval from Sheep’s milk with 3.88% of fat, with Traditional technology – industrial could be produced, production with desirable organic tasting (organoleptic) for consumer and market.

Key Words: Milk, coagulum, whey, curd, cheese, Kačkaval.

Introduction

The suitability of milk as a raw material for production of cheese depends largely on conditions at the dairy farm. Quite a part from the general demand for strict hygienic conditions, milk from sick sheep or animals undergoing treatment with antibiotics must not be used for cheese making, or any their milk product. Feeding animals on badly prepared silage can adversely affect the quality of several varieties of cheese.

The first cheese may have been made by people in the Middle East or by nomadic Turkic tribes in Central Asia. Since animal skins and inflated internal organs have, since ancient times, provided storage vessels for a range of foodstuffs, it is probable that the process of cheese making was discovered accidentally by storing milk in a container made from the stomach of an animal, resulting in the milk being turned to curd and whey by the rennet from the stomach. There is a legend with variations about the discovery of cheese by an Arab trader who used this method of storing milk.

Cheese is a fermented food derived from the milk of various mammals. Cheese is a generic term for a diverse group of milk-based food products. Cheese is produced throughout the world in wide-ranging flavours, textures, and forms. Cheese consists of proteins and fat from milk, usually the milk of cows, buffalo, goats, or sheep. It is produced by coagulation of the milk protein casein. Typically, the milk is acidified and addition of the enzyme rennet causes coagulation. The solids are separated and pressed into final form. Some cheeses have moulds on the rind or throughout. Most cheeses melt at cooking temperature.

Hundreds of types of cheese are produced. Their styles, textures and flavours depend on the origin of the milk (including the animal's diet), whether they have been pasteurized, the butterfat content, the bacteria and mould, the processing, and aging.

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Herbs, spices, or wood smoke may be used as flavouring agents. The yellow to red colour of many cheeses is from adding annatto.

Cheese is valued for its portability, long life, and high content of fat, protein, calcium, and phosphorus. Cheese is more compact and has a longer shelf life than milk. Cheese makers near a dairy region may benefit from fresher, lower-priced milk, and lower shipping costs. The long storage life of some cheese, especially cheese that encased in a protective rind, allows selling when markets are favourable.

Production of cheese goes through different phases that are common to all of cheese sorts. There are also other ways of treatment, which are specific to certain varieties. During the rest of the curd making process the bacteria grow and form lactic acid, and the curd grains are subjected to mechanical treatment with stirring tools, while at the same time the curd is heat up according to prearranged programmed.

The combined effect of these there actions – growth of bacteria, mechanical treatment and heat treatment – results in sunrises, i.e. separation of whey from the curd. The finished curd is placed in cheese moulds of metal, wood or plastics, which determines the shape of the finished cheese.

There are many factors that can affect milk composition, such as breed variations, sheep to sheep variations, herd to herd variations, including management and feed considerations, seasonal variations, and geographic variations and global warming. The necessity of studying Kačkaval cheese at conditions of Kosovo has been explained not only by its market demand but most of all by the geographic possibilities for its production growth in this country from sheep fresh unpasteurized milk.

The answer to this interest requires a profound analyzing of the physical and chemical composition and technological properties of milk produced in Kosovo. On the basis of this, the suitable parameters of the preferred variant of Kačkaval cheese, according to the climatic peculiarities of the country should be established, which will be a contribution for the development of milk processing science and practical application of Kosovo. Peculiar future of organic tasting (organoleptic) for estimation of cheese Kačkavall from sheep fresh unpasteurized milk with Traditional technology – industrial could be produced, production with desirous organic tasting (organoleptic) for consumer and market (Đjordjevic, 1987; Luqet, 1990; Maxhuni, 2009; Petrovic, 1984).

Materials and Method

It’s used fresh milk to produce cheese of Kačkaval - unpasterized Sheep’s with these parameters. For physical-chemical peculiar feature of milk and Kačkaval samples were used this method: Soxhelt-Henkels method were used to define sour taste $^8$H, for definition of pH value were used the pH-meter, Miskra, Kranj, Type MA 5730, for definition of milk density g/cm$^3$ were used Laktodezimetre, for definition of fat percentage % we use the method of Gerber, in defined of dry matters until drying up of constant mass, dry quantity of mass without fat has been done in calculated way.

Percentage of fat at dry mass has been done in calculated way, water quantity has been done in calculated way, for definition of general Nitrogen (N), were used the Kjeldahs method, for definition of saline’s (NaCl) were done according to the IDF standards, beside, equipments and devices which are provided with regulations to define the physical-chemical peculiar feature of milk and cheese were used as well the below mentioned: Technological line for production of Kačkaval cheese, consist from: two fold bath with capacity of 5000 l (Nederland’s bath equipped with equipment for benefit ion of coagulant-dough mass-curd), Coagulant baking line – “Maxhar” Budapest, Hungarian frames, shelves.

Feeding animals on badly prepared silage can adversely affect the quality of several varieties of cheese.

When collection of milk on alternate days was introduced, cheese producer who had to use such milk noticed that the quality of cheese frequently deteriorated. This tendency was particularly noticeable when the milk had to be stored a further day after reception, even when it was chilled to 4°C in conjunction with transferor from road tanker to storage tank.

During cold storage, the milk protein and milk salts conge character, which tends to impair cheese-making properties. It has been shown that about 25% of the calcium precipitates as phosphate after 24 hours storage at $+5^\circ$C. This reduction, however, is temporary; when the milk is pasteurized, the calcium redisovers and the coagulating properties of the milk are almost completely restored. $\beta$-
Casein also leaves the complex casein micelle system during cold storage, which further contributes to reducing the cheese making properties. However, this reduction too is almost completely restored by pasteurization.

Another and equally important phenomenon is that the micro flora introduced into the milk by recontamination especially Pseudomonas spp. - will adapt to the low temperature at which the enzymes, proteins and lipases, will decompose protein and fat respectively. The result of such action is a “bitter” flavour emanating from decomposition of the β-casein that has left the casein micelle during low – temperature storage.

Cheese has been made in most cultures from ancient times. Cheese is a milk concentrate, the basic solids of which consist mainly of protein, actually casein and fat. The residual liquid is called whey. As a rule of thumb, the casein and fat in the milk are concentrated approx. 10 times in production of hard and semi-hard types of cheese. No strict definition of the concept of cheese is possible, as so many variants exist.

The fact for this product is that has found nice place in milk industries in Kosova. Peculiar future of organic tasting (organoleptic) for estimation of cheese Kaçkaval from sheep’s milk with 3.88% of fat, with traditional technology – industrial could be produced, production with desirous organic tasting (organleptic) for consumer and market.

Production of cheese goes through different phases that are common to allot of cheese sorts. There are also other ways of treatment, which are specific to certain varieties. Cheese milk is pretreated, possibly premiered after addition of a bacterial culture appropriate to the type of cheese, and mixed with rennet. The enzyme activity of the rennet causes the milk to coagulum. This mass is cut with special cutting tools into small cubes (1x1 cm) of the desired size – above all to enable share-out the whey.

During the rest of the curd making process the bacteria grow and form lactic acid, and the curd grains are subjected to mechanical treatment with stirring tools, while at the same time the curd is heat up according to prearranged programmed.

The combined effect of these there actions – growth of bacteria, mechanical treatment and heat treatment – results in sunrises, i.e. separation of whey from the curd. The finished curd is placed in cheese moulds of metal, wood or plastics, which determines the shape of the finished cheese.

The cheese is pressed, either by its own weight or more commonly by applying pressure to the moulds. Treatment during curd making and pressing determines the characteristics of the cheese. To produce Kaçkaval type of hard cheese; unpasteurized (fresh) milk was used.

It was made three producing experiments of this cheese kinds and taken three samples of Kaçkaval for experiment (every seventh baked cheese roundel was taken as a sample). For jellification-milk coagulation were used yeast, where 2g. Of yeast in temperature of 30°C jellification-coagulate 100 l. of milk in 40º minutes. From every cheese product were taken in parallel two samplings (viz 2 x 3= 6 samples) which were analyzed:

Physical-chemical peculiarity, in time term of one day long, fifteen days and thirty days. After 40-ty minutes milk coagulates. Coagulant will be cut up in 1x1 cm. As coagulation Kaçkaval was produced by cow’s milk and experimented in Dutch vat with capacity from 5000 l, with 3.88% of fat. Milk is boiled in temperature of 33ºC, well intermixing afterwards adding ferment-yeast (100 gr. of yeast will be dissolved in three litters of watt goes down to the bottom of the vat, then the whey goes away through rubber pipe.

Coagulated part will be intermixed for 15-in minutes and heated in temperature of 42º C with warm water where in this temperature will be mixed for 40-ty minutes. Afterwards whey will be separated and fresh coagulum (curd remains) in the vat. Curd will be cut up in bulks fro 15-30 cm where is baked in surroundings temperature (usually at 24º C) about 16 hours. Cheese is baked in briny water (with 15%) in 75º C, after coagulant goes through the grind machine and forming of this mass under the pressure-pressing and filling up the shapes. Cheese remains in surroundings temperature in the shape (usually at 25º C) about 24 hours (in the meantime the shapes with the cheese should be whirled).

After removing the cheese from the shapes they stay to be dried up for one day in the same surroundings temperature (in the same room), after that they are delivered to waiting room for dry salting that takes two weeks (where each day the cheese is whirl about).

The cheese is baked for thirty days in temperature up to 20ºC, as well as on moisture up to 85%.
The cheese is moistened in the store (the cheese is whirl about, salted and cleaned) (Coralba, 1982; Sabados, 1996; Gosta, 1995; Anonym., 1980; Havranek & Kirin, 1996; Anonym., (1983).

Table 1. The physical – chemical analysis results of sheep milk

<table>
<thead>
<tr>
<th>Sample</th>
<th>pH</th>
<th>%SH</th>
<th>Density g/m³</th>
<th>Fat %</th>
<th>Mat. sec %</th>
<th>Mat. sec without % fat</th>
<th>Water %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
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<td>4.00</td>
<td>9.53</td>
<td>5.53</td>
<td>90.47</td>
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<td>10.74</td>
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<td>89.26</td>
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Table 2. The results of physical – chemical peculiarity of Kaçkaval cheese produced by sheep’s Milk during one day baking

<table>
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<tr>
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<th>pH</th>
<th>%SH</th>
<th>Fat %</th>
<th>Mat. sec %</th>
<th>Mat. sec without % fat</th>
<th>Solids (NaCl) %</th>
<th>N general %</th>
<th>Prot. gene %</th>
<th>Water %</th>
</tr>
</thead>
<tbody>
<tr>
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<td>25.96</td>
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<td>4.54</td>
<td>28.37</td>
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</tr>
<tr>
<td>X</td>
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<td>59.00</td>
<td>22.53</td>
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<td>1.23</td>
<td>4.67</td>
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Table 3. The results of physical – chemical peculiarity of Kaçkaval cheese produced by sheep’s Milk during fifteen days baking

<table>
<thead>
<tr>
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<th>pH</th>
<th>%SH</th>
<th>Fat %</th>
<th>Mat. sec %</th>
<th>Mat. sec without % fat</th>
<th>Solids (NaCl) %</th>
<th>N general %</th>
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<td>18.53</td>
<td>50.00</td>
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<td>4.59</td>
<td>28.68</td>
<td>50.00</td>
</tr>
<tr>
<td>X</td>
<td>4.76</td>
<td>55.60</td>
<td>22.53</td>
<td>52.31</td>
<td>29.78</td>
<td>2.58</td>
<td>4.67</td>
<td>29.18</td>
<td>47.69</td>
</tr>
</tbody>
</table>

Table 4. The results of physical – chemical peculiarity of Kaçkaval cheese produced by sheep’s milk during thirty days baking

<table>
<thead>
<tr>
<th>Sample</th>
<th>pH</th>
<th>%SH</th>
<th>Fat %</th>
<th>Mat. sec %</th>
<th>Mat. sec without % fat</th>
<th>Solids (NaCl) %</th>
<th>N general %</th>
<th>Prot. gene %</th>
<th>Water %</th>
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<td>56.80</td>
<td>31.30</td>
<td>2.92</td>
<td>6.36</td>
<td>39.75</td>
<td>43.20</td>
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<tr>
<td>2</td>
<td>4.95</td>
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<td>24.10</td>
<td>50.14</td>
<td>26.04</td>
<td>2.51</td>
<td>6.15</td>
<td>38.43</td>
<td>49.86</td>
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<td>50.00</td>
<td>19.53</td>
<td>50.00</td>
<td>30.47</td>
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</tr>
<tr>
<td>X</td>
<td>4.97</td>
<td>51.60</td>
<td>24.04</td>
<td>52.31</td>
<td>29.27</td>
<td>2.76</td>
<td>5.96</td>
<td>37.25</td>
<td>47.69</td>
</tr>
</tbody>
</table>

Valuation of organoleptic experimental cheese samples were don according to Regulation for evaluation of milk and milks products, Novi Sad 1980. The evaluation he’s been done by five members and samples were valuated with points (2).
PROCESSING DIAGRAM OF KAÇKAVAL CHEESE

Sheep’s fresh raw milk not-pasteurized (5000 l, with 3.88% of fat)

Sampling for milk analysis

Cooling of milk to 33°C (Vat during stirring)

Milk-culture castaway (100 gr remover in 3 l of water)

During incubation (40 minutes)

Processing of Coagulation (cutting gently breaks the curd up into grains into Grains with a size 1x1 cm)

Sampling - Extraction - expulsion of whey – sunrises

(Vat during whey drainage)

Curd manufacture

Add warm water in jacketed cheese

Recolling of Coagulum exudation (drying of coagulum in 42°C)

Sampling - Extraction - expulsion of whey - Leaven castaway

(Vat during whey drainage)

Curd making

Cutting curd (in size 17x30 cm)

Chedderization - Drying of curd (in ℃ 24°C about 16 hours)

Cheese baking - Baking curd in Delicatessen (Salamura) with 15% NaCl, In ℃ 75°C, long 2 - 3 minutes

Moldiness of cheese

Cheese packaging (with mould in ℃ 25°C, between 24 hours)

Drying of cheese one day in ℃ 20°C

Salting of cheese in ℃ 20°C between two weeks

Drying of cheese in ℃ 20°C, with 85% of humidity, between one month

Cheese preservation

Diagram.1. Processing diagram of kaçkaval cheese
Table 5. Organoleptic results for evaluation of cheese produced by sheep’s milk after thirty days

<table>
<thead>
<tr>
<th>Ingredients</th>
<th>Average number of points</th>
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<tbody>
<tr>
<td>Externals</td>
<td>3</td>
</tr>
<tr>
<td>Colour</td>
<td>3</td>
</tr>
<tr>
<td>Consistency</td>
<td>3</td>
</tr>
<tr>
<td>Cutting</td>
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<tr>
<td>Smell</td>
<td>3</td>
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<tr>
<td>Taste</td>
<td>8</td>
</tr>
<tr>
<td><strong>Total number of points</strong></td>
<td><strong>23</strong></td>
</tr>
</tbody>
</table>

**Results and Discussion**

Three experiments were done with 5000 l of sheep’s fresh non-pasteurized milk (with 3.88% fat). The samples of milk and cheese produced in industrial way by traditional technology were taken to be analyzed from sheep’s milk; the chemical-physical peculiar analysis has been done for fresh milk and fresh cheese lasting from one day, fifteen day and thirty days.

In addition, the analyses were taken for Saline percentage % (NaCl), total percentage of Nitrogen, and total percentage of proteins in cheese. The samples of every seventh roundel have taken to analyze. The 102 analyses were done. I have used the best method to produce this kind of cheese.

Chemical-physical peculiarity results of sheep’s milk produced and stored cheese Kačkavall per one day mil: pH = 6.23, $\theta$ SH = 14.93, density = 1.0297 kg/m$^3$, fat = 3.88%, matter sec = 10.74%, matter sec without fat = 6.86, water = 89.26%.

Chemical-physical peculiarity results of sheep’s milk produced and stored cheese Kačkavall per one day are pH = 4.69, $\theta$ SH = 59.00, fat = 22.53%, matter sec = 51.85, matter sec without fat = 29.31%, saline (Na Cl) = 1.23%, total nitrogen = 4.67%, total proteins = 29.18%, water = 48.15%.

Chemical-physical peculiarity results of sheep’s milk produced and stored cheese Kačkavall for fifteen days are pH = 4.76, $\theta$ SH = 55.60, fat = 22.53%, matter sec = 52.31, matter sec without fat = 29.78%, saline (Na Cl) = 2.58%, total nitrogen = 4.67%, total protein = 29.18%, water = 47.69%.

Chemical-physical peculiarity results of sheep’s milk produced and stored cheese Kačkavall for thirty days are pH = 4.97, $\theta$ SH = 51.60, fat = 24.04%, matter sec = 52.31, matter sec without fat = 29.27%, saline (Na Cl) = 2.76%, total nitrogen = 5.96%, total protein = 37.25%, water = 47.69%.

During the production of cheese, very important role takes the sort and the quality of milk. As percentage of fat in milk changes so the percentage of fat in cheese changes also in matter sec, proteins, saline and water are changes too. There are opportunities for technological and industrial production cheese combined with milk, to meet the needs of the market.

With this type of milk, consumers would be ken possibility of consuming types of cheese with a joint production. It is ascertained that during baking-drying of cheese in the store, from the first day until the thirteen day the physical-chemical parameters are raising, such as raising percentage of matter sec, total nitrogen (N), saline (NaCl) and in very small percentage the percentage quantity of fat.

Organoleptic valuation of kaçkaval after thirty days it was ascertained it has achieved the peculiarity of smell, taste, consistency because in general it has achieved very good estimation. With traditional technology and with good quality of milk we can have a good product of this kind of cheese with very good organoleptic peculiarity: nice smell, good taste and strong cheese.

In normal standards is needed 10 litters of milk to produce 1 kg cheese of this kind. By means of this method, for one kg Kačkaval cheeses were used 8 litters of un-standardized and un-pasteurized fresh milk.

After thirty days, cheese is prepared for the trade. Production of this kind of cheese has nutritious value for the population and good economic value for milk industry considering profit of one kg cheese. The economic parameters are improved. This kind of cheese can hold out in surroundings temperature to 25°C, as well as on moisture up to 85%.

Normally for this cheese we must wait forty days for market. But with this processing diagram of Kačkavall cheese, we can give this kind of cheese for market for thirteen days.

**Acknowledgment:** We thank all the friends, who were helped in realizations of this research.
References
Anonym., (1983) Pravilnik o kakvoci mlijeka, mljecnih proizvoda, sirila i cistih kultura, Sluzbeni list SFRJ, br. 32.
Long-Term Dispersion Pattern of SO₂ in the Neighbourhood of Thermal Power Stations at Neyveli, India

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Abstract: The air quality models play a major role for prediction in the field of air quality management by establishing the relationship between the source emission and receptor point concentration. The estimation of long term average concentrations of pollutants is essential for environment management and planning. To estimate probable air quality, the meteorological data by CARD NLC were used for concentration prediction with the help of newly developed long – term Gaussian plume model (MPC_LP). The present study deals with long –term dispersion pattern of pollutants in the neighbourhood of Thermal power plants at Neyveli. This study also includes computations of seasonal averages of SO₂ concentrations at downwind locations under various computations of wind speed and atmospheric stability classes. The spatial pollution rose pattern of SO₂ concentration for different seasons were developed over an area of size 37 km X 31 km with an interval of 1 km X 1 km in and around the Thermal Power Plants. The SO₂ isopleths indicated the probable zones of maximum concentration of sulphur dioxide in a particular season over town ship, industrial and agricultural rural areas.

Key words: Sulphur dioxide, Long Term average concentration, pollution rose, dispersion pattern, isopleths

Introduction

The Thermal power plants are located in the Latitude of 11° 28’ and 11° 37’ N, longitude of 79° 25’ and 79° 33’E at Neyveli. Neyveli Lignite Corporation (NLC) is one of the most industrialized and thickly populated townships (please see the Figure 1). Thermal power generation is the largest source of SO₂ in the rural area besides other industrial processes. NLC houses two mines and two thermal power stations. Thermal power stations-II is designed for 7 numbers of boilers producing electricity of generation power at 210 MW each, using lignite as the fuel. The emission from a single unit of 210 MW capacities is considered in the Gaussian diffusion equation, for predicting ground level downwind concentrations. Power plants, in the contemporary India, experience a profound change in the nature and extent of air pollution. Factors such as industrial expansion, accelerated consumption of products, the introduction of new chemical processing industries, the vastly increased use of automobiles and growth of urbanisation, have all greatly increased the demand of energy. In order to meet out the energy demand, power generation activities have been steered in that in-turn increases the volumes of pollutants thereby presenting new threats to the human health, animal health, plant life, property value and the environment. However, a sporadic development of industries has sprung up in the neighbourhood of residential areas in India. As a result, the magnitude and severity of air pollution problems have been attracted by the attention of the public. Therefore, there is a necessity to adopt a systematic procedure for knowing the dispersion pattern of pollutants emitted from each industry located in the area, in order to maintain the ambient air quality in and around the industries, within the safe limits. Isopleths would offer the necessary information for evolving the relationship between the emission rate and the resulting air concentration of a specific pollutant on the spatial.

Materials and Methods

Model

Many number of dispersion models available to determine the spatial and temporal variations of pollutants in the ambient air environment. A recommended model that comprises the Gaussian
diffusion equation to calculate the concentration of SO$_2$, which is emitted from continuous elevated sources (Goyal & Singh, 1990). The newly self designed computer aided Gaussian dispersion model namely Multiple Point source Complex Long term Period (MPC_LP) has been used to estimate the monthly / seasonal average SO$_2$ concentrations by using the following equations, which is extensively described by (Turner, 1967, 1944; ISO, 1978; Department of Environment 1983).

\[
\chi(\text{long-term average}) = \left[ \frac{2}{\pi} \right]^{3/2} \frac{0.01fQ^11 \times 10^6}{U \sigma_z \left( \frac{2\pi z}{n} \right)} \exp \left( -\frac{H^2}{2\sigma_z^2} \right) \exp \left( -\frac{y^2}{2\sigma_y^2} \right) \ldots (1)
\]

Where $\chi$ = long-term average concentration ($\mu$g/m$^3$);
$Q^1$ = emission rate of the $k^{th}$ source (g/s),
f = the frequency of wind in percent,
$U$ = the average wind speed;
$\sigma_z$ = the standard deviations of the plume concentration in the vertical direction;
$\sigma_y$ = the standard deviations of the plume concentration in the horizontal direction;
$H$ = effective stack heights (m),
y = crosswind distance (m).
x = the downwind distance (m);
$n$ = number of direction sector and \( \{2\pi x/n\} \) is the sector width.

According to this equation, the long term average SO$_2$ concentration at receptor point is sum of the contribution of the sources due to meteorological conditions recorded in the area, each multiplied by its frequency of occurrence in the long term.

**Model parameterization**

Gaussian Dispersion Equation (GDE) involves various parameters such as wind speed at stack heights, dispersion coefficients, and plume rise etc. Many investigations such as Pasquill (1961), Turner, (1964, 1967), Munn, (1966), and Briggs, (1973), have made studies on classifying stability classes in the absence of any sophisticated observations. The meteorological conditions, defining
Pasquill turbulence types, have been suitably modified and it has been chosen for the present study. The diffusion co-efficient is estimated through various approaches made by many researchers (Smith, 1951; Smith, 1968; Pasquill, 1961, 1962; Gifford, 1961; Turner, 1964; Carpenter et al., 1971; Briggs, 1973). If the physical stack height is higher than 100 m, Briggs’ interpolation schemes give better estimate. Therefore, Briggs’ (1973) proposes a series of interpolation formulas that have been used in the Gaussian diffusion equations for estimating $\sigma_Y$ and $\sigma_Z$. Several investigators who have proposed formulae for the estimation of plume rise, are Briggs (1971, 1973), Gulberg, 1975, Montogomery, (1973), Holland, (1995), Swamy, (1996). Of all the formulae, the theoretical formula by Briggs (1971, 1973) yields the best results. Hence, this formula is used for estimating the plume rise. Averaging time is necessary to estimate concentrations from a single source for time intervals greater than a few minutes; the best estimate apparently can be obtained from (Turner, 1994): The MPCLP model has utilized the power law co-efficient ‘$p$’ as 0.41. The pollution is assumed to be non reactive and its removal and transformation rates are not considered. The site is terrain is assumed to be flat and the height of the receptor is at the ground level.

**Input Parameters**

Neyveli is an industrial area with densely populated township located on the south of the Cuddalore city. The residential areas of the city are situated to N-NE of the power plant, while the agricultural areas are S-SW of the industrial location, the mining zone, power plant and its boundary of the industrial as shown in the study area map (please see Figure 1). The data requirements for dispersion analysis consisted of two important parts: the emission inventory and the meteorological data. In order to determine the pollutant level in the agricultural rural areas, which is mainly surrounded the thermal power plant; two crop seasons namely Kharif crop and Rabi crop have been selected. The Kharif crop season lying between third week of October to end of February and Rabi crop season is from second week of May to middle of September in every crop year.

**Emission Data**

The Thermal Power Stations include about seven stacks in Thermal Power Station – I and five stacks in Thermal Power Station – II that are responsible for SO$_2$ emission in the area. Figure 1 shows the stack coordinate, stack height, exits stack diameter, emission rate of SO$_2$, exit stack velocity and exit stack gas temperature. Typical hourly emission files for the all emission stack have been prepared for a year, which is gathered from CARD, (NLC). Thus, the emission from each stack is available.

**Meteorological Data**

The annual meteorological monitoring data gathered for the year 2008 from CARD, Neyveli, in order to observe the prevailing weather in and around N.L.C campus. Anemometer was fixed at the roof - top of a three storeyed building at Neyveli, in such a way that the observation height was about 10 m above the ground level. During the period of observations, wind velocity, wind directions, dry bulb temperature, wet bulb temperature, cloud cover, etc., were measured. The wind rose diagram was constructed for the year 2008 season both Kharif and Rabi meteorological data (please see Figures 2a & 2b). Wind rose frequency and stability distribution for Kharif crop season and Rabi crop season also shown in figure 3a and 3b respectively for the year 2008. The seasonal meteorological data for the year 2008 is given in Table 1a and 1b. The mixing height can be determined by various methods available using temperature profiles measured on the fixed tower or by sonde and the remote sensing techniques. In this study, the mixing height is determined by using the method based on temperature profile.

It is seen quite often that the measures wind speed is less than 1m/s. It is very clear that Gaussian models grossly over predict concentrations under low wind speed condition if the conventional values for $a$ and $b$ appropriate to each pasquill’s stability class are used (Goyal & Singh, 1990). Also, contributions to long term concentration during calm conditions are usually neglected. Thus, it is assumed that in this study, all directions are equally probable and the mean wind speed associated is 0.25 m/s.
Figure 2a. Wind rose for the Kharif crop season, 2008

Figure 2b. Wind rose for the Rabi crop season, 2008

Figure 3a. Wind rose frequency and stability distribution for Kharif crop season, 2008

Figure 3b. Wind rose frequency and stability distribution for Rabi crop season, 2008

Table 1a. Frequency table for the meteorological data of the year 2008 (Kharif season)

<table>
<thead>
<tr>
<th>Wind Direction</th>
<th>Wind speed 0.5&lt;2.1 m/s</th>
<th>Wind speed 2.1 - 3.6 m/s</th>
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<td></td>
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<td>B</td>
<td>D</td>
</tr>
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<td>337.500</td>
<td>0.72</td>
<td>0.54</td>
<td>0</td>
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</table>
Table 1b. Frequency table for the meteorological data of the year 2008 (Rabi season)

<table>
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<tr>
<th>Wind Direction</th>
<th>Wind speed 0.5-2.1 m/s</th>
<th>Wind speed 2.1 - 3.6 m/s</th>
<th>Wind speed 3.6 - 5.7 m/s</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>B</td>
<td>0.70</td>
<td>0.31</td>
<td>0.23</td>
</tr>
<tr>
<td>C</td>
<td>0.16</td>
<td>0.16</td>
<td>0.78</td>
</tr>
<tr>
<td>D</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>E</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>F</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

Result and Discussion

The MPC_LP model software was run using the emissions from the stacks of the thermal power plants using grid areas. The area covering the grid area of 480 km² with 1147 receptors comprises of single cells of 1 km². The used grid defined coordinates in terms of X and Y axis, contains selected source and receptor location. Neyveli thermal power plants have two stacks TS-I and TS-II. The TS-I stacks consists of seven chimneys and TS-II stacks consists of five chimneys with different heights, collectively referred to as multiple point source industrial complex. The number of points considered for the grid includes 37 on the X-axis which has a total length 37 km, with a spacing of 1 km between two points and 31 on the Y-axis, which has a total length of 31 km and spacing of 1 km between points. Collectively this makes up 1147 receptor, in a uniform Cartesian grid. Therefore, the grid arrangement has been made to the geographical shape of dimension of Neyveli power plants region. The closest residential area, located at a distance of 6.2 km from NE direction of TS-II and 2 km from north of TS-I plant.

Table 2 shows the SO₂ emission rate from the power plants for the year 2008. For the model validation purposes, the predicted concentrations are compared with the actual real time measured concentration for sulphur dioxide, from the 27 monitoring stations in the neighbourhood of Neyveli thermal power plants. Figure 4 shows the slope of the predicted seasonal average SO₂ concentrations against the observed values which is equal to 0.822. This proves the accuracy of the model.

![Figure 4](image-url)
For this study, the seasonal long term average ground level SO$_2$ concentrations at all the grids of 37 x 31 Km in the spatial area of NLC with an interval of 1 km was computed with the help of MPCLP model. The pollution rose was drawn for the two crop seasons with the help of the SURF Software. The spatial distribution of long term ground level SO$_2$ concentrations for the 2008 seasons both Kharif and Rabi crop seasons are presented in Figure 4a, 4b and 5a, 5b respectively. The sources of emission of SO$_2$ as 856.025 X 10$^6$ $\mu$g/s in the computations using expression 1 for multiple point sources.

The model describes the long term seasonal pollution rose realistically. The Highest seasonal average maximum concentration of sulphur dioxide is 55.60 $\mu$g/m$^3$ during the kharif season, at 1.8 km from the power plants in south west direction. In Rabi season, the maximum average sulphur dioxide is 48.83 $\mu$g/m$^3$ found in north east direction at 6.2 km from power plants. In Kharif season, the predominant wind force was identified towards south west direction (see Figure 2a) while North – Northeast direction in Rabi season (see Figure 2b).
Table 2. A Typical Hourly Emission File for MPCLP

<table>
<thead>
<tr>
<th>Xs (m)</th>
<th>Ys (m)</th>
<th>Q(μg/m³)</th>
<th>hs (m)</th>
<th>ts (°C)</th>
<th>Vs (m/sec)</th>
<th>ds (m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0000</td>
<td>0.0000</td>
<td>856.025</td>
<td>170.000</td>
<td>423.000</td>
<td>25.000</td>
<td>4.850</td>
</tr>
<tr>
<td>-0.1000</td>
<td>-0.1000</td>
<td>856.025</td>
<td>170.000</td>
<td>423.000</td>
<td>25.000</td>
<td>4.850</td>
</tr>
<tr>
<td>-0.2000</td>
<td>-0.2000</td>
<td>856.025</td>
<td>170.000</td>
<td>423.000</td>
<td>25.000</td>
<td>4.850</td>
</tr>
<tr>
<td>-0.3000</td>
<td>-0.3333</td>
<td>830.250</td>
<td>220.000</td>
<td>423.000</td>
<td>25.000</td>
<td>4.850</td>
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<tr>
<td>-0.4000</td>
<td>-0.4444</td>
<td>830.250</td>
<td>220.000</td>
<td>423.000</td>
<td>25.000</td>
<td>4.850</td>
</tr>
<tr>
<td>-0.5000</td>
<td>-0.5000</td>
<td>830.250</td>
<td>220.000</td>
<td>423.000</td>
<td>25.000</td>
<td>4.850</td>
</tr>
<tr>
<td>-0.6000</td>
<td>-6.0000</td>
<td>830.250</td>
<td>220.000</td>
<td>423.000</td>
<td>25.000</td>
<td>4.850</td>
</tr>
<tr>
<td>4.1000</td>
<td>3.5000</td>
<td>764.1665</td>
<td>60.000</td>
<td>423.000</td>
<td>16.000</td>
<td>5.100</td>
</tr>
<tr>
<td>4.0000</td>
<td>3.5000</td>
<td>733.6665</td>
<td>60.000</td>
<td>423.000</td>
<td>16.000</td>
<td>5.100</td>
</tr>
<tr>
<td>3.9000</td>
<td>3.5000</td>
<td>771.3333</td>
<td>60.000</td>
<td>423.000</td>
<td>16.000</td>
<td>5.100</td>
</tr>
<tr>
<td>3.8000</td>
<td>3.5000</td>
<td>747.2083</td>
<td>120.000</td>
<td>423.000</td>
<td>16.000</td>
<td>5.100</td>
</tr>
<tr>
<td>3.7000</td>
<td>3.5000</td>
<td>830.250</td>
<td>220.000</td>
<td>433.000</td>
<td>20.100</td>
<td>5.100</td>
</tr>
</tbody>
</table>

It is obvious that the presented isopleths diagram for Kharif season had high concentration in downwind (S-SW) and upwind (N-NE) directions. Similarly the presented isopleths diagram for Rabi season had high concentration in downwind (NE) and upwind (SW) directions. The predicted values also confirm the expected bearing from north. The predicted highest seasonal average concentration was in the range of 40 to 58 (μg/m³). The seasonal average National Ambient Air Quality (NAAQ) standards (India) limit for sulphur dioxide concentrations is 50 μg/m³ in industrial zone, residential area and the rural areas. The 24 hrs maximum concentration of sulphur dioxide is 80 μg/m³. Therefore, residential areas like Neyveli township and other areas in the same direction are at a safe distance from the area of influence. The predicted highest seasonal average sulphur dioxide concentration is 40 μg/m³ (Rabi season) but in Kharif crop season the other rural area’s predicted concentration exceed the NAAQ limits. Since, the neighbourhood of power plants rural area ensuring minimal impact on the habitual or uninhibited areas. Thus, the study can be concluded that the model generates reliable and useful data, which can effectively be used for the prediction of pollutant concentrations from different emission sources.

Conclusions

Emission inventories from the major thermal power generation facilities at Neyveli have been analysed with seasonal variation. Meteorological data for the year 2008 were obtained from the CARD Neyveli and used as input in REMSPACE software to determine stability class and upper air data to generate compatible data file for implementation of the dispersion model. Along with this data, all other specifications such as source point coordinates, stack characteristics, flue gas flow, and exit temperature and exit velocity at stack tip with local terrain detail were fed to the Multiple Point source Complex for Longer Period dispersion (MPC_LP).

The computed results for SO₂ inventories have been discussed in details. The seasonal average predicted SO₂ concentrations were compared with measured air quality monitoring data to validate the model output. It was concluded that seasonal average SO₂ concentrations has large number of rural areas under exceedance from Neyveli power plants but the annual mean predicted SO₂ concentrations (45.63 μg/m³) had with in the NAAQ standards limits.

References:


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Modification Methods for the Enhancement of Adsorption Capacity of Adsorbents: A Review

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Abstract: In this article, modification methods and its enhancement affect on the adsorption capability of various adsorbents for treatment process has been reviewed. Instead of using commercial activated carbon, researchers have studied on the modification of low cost and locally available materials such as agricultural by-products, clays, zeolites, and other adsorbents to have more active surfaces and adsorption capacity. Modifications in literature focused on the four basic methods such as physical, physiochemical, chemical and biological activation. Adsorption capacities of adsorbent have increased quietly as a result of modification.

Keywords: Modification, adsorbent, activation, adsorption capacity

Introduction

Treatment requirements of pollutants especially toxic metals and dyes have been increased since industrialization age and continue to increase today. Therefore, a lot of treatment methods have been developed to overcome these problems including chemical precipitation (Lai and Lin, 2003), biological treatment (Zhang et al., 2009), oxidation (Devi et al., 2009), ion exchange (Cardoso et al., 2004), filtration (Yang et al., 2002) and adsorption (Argun and Dursun, 2008). Adsorption processes have a promising potential for removing pollutants from wastewaters. However, high investment and operational cost of conventional adsorption systems have tended scientists to develop abundantly available, low cost natural adsorbents. Nevertheless, it was observed that a lot of natural adsorbents have some disadvantages such as leading to chemical oxygen demand due to soluble organic constituents and low surface area. As a result of these problems some modification techniques have been studied including physical, physiochemical, chemical and biological activation. Some examples of these methods are investigated and summarized below.

Modification of adsorbent with different methods

Physical and physiochemical activation

Physical treatment may contain oven drying to 105°C, washing with dilute acids for removal of impurities and thermal cracking of the sample at very high temperatures with or without activation reagents. Some examples of physical and physiochemical activation given in Table 1 were as follow; oxygen non-thermal plasma which was produced by dielectric barrier discharge under atmospheric pressure have been used for improving metal adsorption capacity of granular activated carbon by Kodama et al. (2002). They were reported that modification decreased the surface area while increasing the concentrations of acidic functional groups. Kütahyalı and Eral (2004) were also used zinc chloride for impregnation of activated carbon after carbonization (500-700°C). Physiochemical activation has increased surface area and adsorption capacities up to 51 mg/g (Kütahyalı and Eral, 2004). Steam activation of sulphurised carbon prepared from bagasse pith have been applied for the removal of Cd(II) in another study (Krishnan and Anirudhan, 2003). The modification caused to increase sulphuric acid groups (-SO₃H) on the activated carbons and increased the adsorption capacity due to electrostatic effects. Demirbas (2004) reported that alkali glycerol delignification have altered the adsorption capability of lignin obtained from beech and poplar woods. Mohan and Singh (2002)
has obtained activated carbon from bagasse as an agricultural waste by treating raw bagasse with concentrated sulphuric acid in an oven at temperature of 150–165°C during 24 h. The carbonized material has been exposed to thermal activation at 800–850°C for 30 min after washing well with double distilled water to remove the free acid. Manju *et. al.* (1998) prepared the impregnated activated carbon for adsorption of As(III) in a batch reactor. They reported that chemical reaction and the formation of low soluble precipitate CuHAsO$_3$ on the carbon surface have dominantly increased the capacity. For another study, activated carbon has prepared from the solvent extraction residue of the kernel-oil at different burn-off levels to enhance of porosity (Galiatsatou *et. al.*, 2002) and showed average adsorption capacity for zinc ions. The effect of demineralization with H$_2$SO$_4$ and oxidation with (NH$_4$)$_2$S$_2$O$_8$ has also studied to increase the capacity. It has been reported that surface oxygen groups, i.e. carboxyls, phenols and lactones were the main groups responsible to the adsorption.

**Table 1. Adsorption capacities (mg/g) of various adsorbents modified with physical or physiochemical methods for heavy metals**

<table>
<thead>
<tr>
<th>Modification Agents</th>
<th>Adsorbent</th>
<th>Sources</th>
<th>Pb$^{2+}$</th>
<th>Co$^{2+}$</th>
<th>Zn$^{2+}$</th>
<th>Cd$^{2+}$</th>
<th>U</th>
<th>As</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnCl$_2$ and Carbonization</td>
<td>Charcoal (Kütahyalı and Eral, 2004)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>50.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Steam, H$_2$S and SO$_2$</td>
<td>Bagasse pith, Beech and poplar woods lignin (Demirbas, 2004)</td>
<td>8 and 9</td>
<td></td>
<td></td>
<td>7 and 8</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Glycerol, NaOH and Heat</td>
<td>Bagasse pitch, Beech and poplar woods lignin (Mohan and Singh, 2002)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>31</td>
<td>38.03</td>
</tr>
<tr>
<td>H$_2$SO$_4$ and Thermal activation</td>
<td>Bagasse pitch, Beech and poplar woods lignin (Manju <em>et. al.</em>, 1998)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>31</td>
<td>38.03</td>
</tr>
<tr>
<td>Thermal steam activation</td>
<td>Olive pulp (Galiatsatou <em>et. al.</em>, 2002)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>34</td>
<td></td>
</tr>
<tr>
<td>Thermal activation, H$_2$SO$_4$ and (NH$_4$)$_2$S$_2$O$_8$</td>
<td>Olive pulp (Galiatsatou <em>et. al.</em>, 2002)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>5</td>
<td></td>
</tr>
</tbody>
</table>

**Chemical activation**

Chemical modification is the most used methods and may contain acidification, alkali treatment, polymerization, oxidation and impregnation of the sample (Table 2). In this purpose, hexadecyl trimethyl ammonium bromide (HTAB) modification (Benkli *et. al.*, 2004), polyacrylamide-grafted polymerizations including sawdust, pine bark, pine cone, tannin gels and hydrous tin (IV) oxide gel (Raji and Anirudhan, 1998; Argun, 2007; Argun *et. al.*, 2009; Nakano *et. al.*, 2001; Shubha *et. al.*, 2001), glutaraldehyde cross-linking and immobilized chitosan on the surface of nanoporous beads (Jeon and Höll, 2003; Liu *et. al.*, 2002) and chelation reactions (Manohar *et. al.*, 2002) have been frequently used to enhance the adsorption efficiency of a lot of adsorbents towards metal ions from aqueous solutions. The graft polymerization are generally constitute from some steps explained by Shubha *et. al.* (2001): 25 g of adsorbent in 300 ml of aqueous solution are mixed with 5 g N,N'-methylenebisacrylamide and 1.5 g potassium peroxydisulphate is added. Then the contents are stirred vigorously at 70°C after addition of 17.5 g acrylamide. Finally, the polymerized product is washed with water and dried at 80°C. In addition to this steps ethylenediamine/HCl (Raji and Anirudhan 1998) and glycidyl methacrylate (GMA) in presence of Fe$_2$O$_3$ (Donia *et. al.*, 2006) could be used for having more functional groups.

Citric acid modification followed by sodium hydroxide treatment for improving of copper adsorption by commercially available activated carbon has been examined by Chen *et. al.* (2003). They were found that the specific surface area reduced down to 34% while the surface functional groups and hydrophilic character of adsorbent surface increased by modification. In another study, tetrabutyl ammonium iodide (TBAI) and sodium diethyl dithiocarbamate (SDDC) have immobilized on the surface of carbonaceous adsorbents (Monser and Adhoum, 2002). The increase of the removal capacity has been determined as a result of exchanging metal ions with the acidic functional groups such as phenolic, carboxylic, lactonic, hydroxyl and carbonyl groups.

Babel and Kurniawan (2004) has been investigated surface modifications of coconut shell charcoal (CSC) and commercial activated carbon (CAC) with oxidizing agents, such as sulphuric acid and nitric acid. Sarin and Pant (2006) also reported the adsorption of Cr(VI) by cross-linking of
eucalyptus bark with formaldehyde to form phenol–formaldehyde copolymer. Thioglycolic acid modified cassava tuber bark wastes (CTBW) have been examined for adsorption (Horsfall Jr. et. al., 2006). The -SH group interaction with bark surface has been found as responsible to increase of adsorption capacity. Another study focused on capacity improvement of the wheat bran by using HCl, H2SO4, HNO3, NaCl (Farajzadeh & Monji, 2004). Complexation, adsorption, ion exchange and size exclusion have been stated as probable adsorption mechanism.

The immobilization of some dyes onto adsorbent surface such as bentonit, groundnut shells, sawdust and jute fibre for enhancement of the adsorption capacity was studied for heavy metal adsorption (Hassanien et. al., 2010; Shukla & Pai, 2005). The azo linkage and the OH groups of reactive dye have been reported as favorable for chelate formation with metal ion. Other similar researches evaluated graft polymerization of glycidyl methacrylate with cellulose based adsorbent in the presence of ceric ammonium nitrate (CAN) initiator (Navarro et. al., 1999) and hydrogen peroxide oxidation (Shukla et. al. 2006). Acidic modification of agricultural by-products and wastes are generally used to elution of phenolic compounds (Costodes et. al., 2003; Argun et. al., 2005; Argun et. al., 2007) and to increase of surface charge and functional groups (Vaughan et. al., 2001). Oxidation can also applied for modification of tree materials (Argun & Dursun, 2008; Argun et. al., 2008).

Denizli et. al.(2003) have been developed new approach to improve of adsorption capacity by using 2-methacryloylamidocysteine (MAC) as a metal-complexing ligand. Thiolate groups were stated as the possible groups to react with cadmium ions. Nitrogen and oxygen atoms on the surface also found responsible to the metal–chelate interactions due to unpaired electrons. Chelating reactions have been frequently used to enhance the adsorption efficiency of a lot of adsorbents towards metal ions from aqueous solutions by Manohar et. al. (2002). It was reported that acid and alkali modification of biomasses leads to disruption of microbial cell walls and solubilization of certain cell constituents such as lipids (Saygideger et. al. 2005; Selatnia et. al. 2004). The sequential treatment of 5% HCl and 50% NaOH with crab shell waste, which contains chitosan, has also reported to improve adsorption capacity for nickel (Pradhan et. al., 2005). Clay and zeolite based adsorbents can be modified by NH4Cl, NaNO3, KNO3 and Ca(NO3)2 (Faghihian and Kabiri-Tadi, 2010), poly(oxo zirconium) and tetrabutylammonium (Gupta and Bhattacharyya, 2006), 2-mercaptobenzimidazole (MBI) (Manohar et. al., 2002), manganese oxides (Al-Debs et. al., 2001) and iron-coating (Lai and Chen, 2001). It has been reported that polymeric modifications did not increase the adsorption capacity while oxidized forms increased probably due to increase of surface area and negative surface charge after modification. Jeon et. al. (2002) has prepared carboxylated alginic acid through oxidation reaction with potassium permanganate and reached high uptake capacity up to 3.1 mmol/g at pH 4. The hydroxyl group of natural alginic acid has been transformed into the carboxylic acid by oxidizing alginic acid with potassium permanganate at 30°C for 30 min. Al-Asheh et. al. (2003) has tested natural and chemically treated chicken feathers to remove copper and zinc from wastewater. Alkaline solutions of 0.2 N NaOH and dodecyl sulphate solution with 0.6 wt%, as anionic surfactant, have found to be the best for the sorption process.

**Biological activation**

Biological modifications of adsorbents are rather rare due to some experimental difficulties. Some results of experimental studies from literature are summarized in Table 3. Ozdemir et. al. (2005) has modified calcium and sodium alginate with an extracellular polysaccharide (EPS) produced by the activated sludge bacterium *Chryseomonas luteola* in their study. They have observed that alginate was converted into hydrogels via cross-linking with divalent calcium ions. Gibert et. al. (2005) has been focused on the potential usage of vegetal compost for the Zn and Cu adsorption in another study. Surface functional groups of -SO2H2 and the existence of monodentate and bidentate metal-binding reactions have been found as probable adsorption mechanism.
Table 2. Adsorption capacities (mg/g) of various adsorbents modified with chemical methods for heavy metals

<table>
<thead>
<tr>
<th>Modification Agents</th>
<th>Adsorbent</th>
<th>Sources</th>
<th>Cu^{2+}</th>
<th>Ni^{2+}</th>
<th>Cr^{3+}</th>
<th>Cr^{6+}</th>
<th>Hg^{2+}</th>
<th>Pb^{2+}</th>
<th>Co^{2+}</th>
<th>Zn^{2+}</th>
<th>Cd^{2+}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyacrylamide</td>
<td>Sawdust</td>
<td>(Raji and Anirudhan, 1998)</td>
<td>12</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Pine bark</td>
<td>(Argun et al., 2009)</td>
<td>45</td>
<td>55</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Citric acid</td>
<td>Activated carbon</td>
<td>(Chen et al., 2003)</td>
<td>14.92</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TBAI and SDDC</td>
<td>Activated carbon</td>
<td>(Monser and Adhoun, 2002)</td>
<td>38</td>
<td>6.8</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>9.9</td>
</tr>
<tr>
<td>Citric acid</td>
<td>Activated carbon</td>
<td>(Argun et al., 2009)</td>
<td>45</td>
<td>55</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nitric acid</td>
<td>Activated carbon</td>
<td>(Liu et al., 2002)</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
<td>0.08</td>
<td>0.08</td>
<td>0.08</td>
<td>0.09</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Formaldehyde and H_{2}SO_{4}</td>
<td>Eucalyptus bark</td>
<td>(Denizli et al., 2006)</td>
<td>90.9</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>83</td>
<td>26</td>
</tr>
<tr>
<td>Thioglycolic acid</td>
<td>Bark wastes</td>
<td>(Farajzadeh and Monji, 2004)</td>
<td>90.9</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NaCl</td>
<td>Wheat bran</td>
<td>(Shukla and Pai, 2005)</td>
<td>14.5</td>
<td>13.3</td>
<td>87</td>
<td>82.8</td>
<td>64</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dye (C.I. Reactive Orange 13)</td>
<td>Groundnut shell</td>
<td>(Shukla and Pai, 2005)</td>
<td>7.6</td>
<td>7.49</td>
<td></td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>Dye (C.I. Reactive Orange 13)</td>
<td>Sawdust</td>
<td>(Denizli et al., 2006)</td>
<td>8.07</td>
<td>9.87</td>
<td></td>
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<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>MAC</td>
<td>Polymer</td>
<td>(Cosides et al., 2003)</td>
<td>91</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>254</td>
</tr>
<tr>
<td>Formaldehyde (HCHO and H_{2}SO_{4})</td>
<td>Sawdust</td>
<td>(Costodes et al., 2003)</td>
<td>22</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NaOH and H_{2}SO_{4}</td>
<td>Lemna minor Streptomyces rimosus</td>
<td>(Saygideger et al., 2005)</td>
<td>69 &amp; 59 &amp;</td>
<td>83 &amp; 25 &amp;</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NaOH</td>
<td>NaOH and formaldehyde</td>
<td>(Nakano et al., 2001)</td>
<td>90.9</td>
<td>150.4</td>
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<td>NaS</td>
<td>Activated carbon</td>
<td>(Goel et al., 2005)</td>
<td>90.9</td>
<td>150.4</td>
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<tr>
<td>HCl and NaOH</td>
<td>Crab shell</td>
<td>(Pradhan et al., 2005)</td>
<td>0.25</td>
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<tr>
<td>HCl</td>
<td>Red mud</td>
<td>(Pradhan et al., 1999)</td>
<td>1596</td>
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<td>ZrO (oxo zirconium)</td>
<td>Montmorillonite</td>
<td>(Gupta and Bhattacharyya, 2006)</td>
<td>10.5</td>
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<td>Tetrabutylammonium (TBA)</td>
<td>Montmorillonite</td>
<td>(Gupta and Bhattacharyya, 2006)</td>
<td>8.5</td>
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<tr>
<td>Methylene blue</td>
<td>Bentonite</td>
<td>(Hassani et al., 2010)</td>
<td>37</td>
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<tr>
<td>H_{2}O_{2}</td>
<td>Jute fibres</td>
<td>(Shukla and Pai, 2005)</td>
<td>7.7</td>
<td>5.6</td>
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<tr>
<td>Fenton oxidation</td>
<td>Pine bark</td>
<td>(Argun and Dursun, 2008)</td>
<td>30</td>
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<td>Fenton oxidation</td>
<td>Pine cone</td>
<td>(Argun et al., 2008)</td>
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<td>C.I. Reactive Orange 13</td>
<td>Jute fibres</td>
<td>(Shukla and Pai, 2005)</td>
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<td>H_{2}O_{2}</td>
<td>Coir fibres</td>
<td>(Shukla et al., 2006)</td>
<td>4.33</td>
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<tr>
<td>Chloroacetic acid, ethylenediamine and carbodiimide</td>
<td>Chitosan</td>
<td>(Jeon and Höll, 2003)</td>
<td>496</td>
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<td>Ceric ammonium nitrate, glycidoxy methacrylate and polyethyleneimine</td>
<td>Cellulose</td>
<td>(Navarro et al., 1999)</td>
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<tr>
<td>HCl</td>
<td>CTAB</td>
<td>Rhizopus nigricans</td>
<td>46</td>
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<tr>
<td>PEI</td>
<td>APTS</td>
<td>(Bai and Abraham, 2002)</td>
<td>50</td>
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Table 2: Adsorption capacities (mg/g) of various adsorbents modified with chemical methods for heavy metals

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<thead>
<tr>
<th>Modification Agents</th>
<th>Adsorbent</th>
<th>Sources</th>
<th>Cu^{2+}</th>
<th>Ni^{2+}</th>
<th>Cr^{6+}</th>
<th>Hg^{2+}</th>
<th>Pb^{2+}</th>
<th>Zn^{2+}</th>
<th>Cd^{2+}</th>
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</thead>
<tbody>
<tr>
<td>Polyacrylamide and carboxylic acid</td>
<td>Hydrous tin (IV) oxide</td>
<td>(Shubha et al., 2001) (Al-Degs et al., 2001)</td>
<td>113</td>
<td>120</td>
<td>72.99</td>
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<tr>
<td>Manganese oxides</td>
<td>Diatomite</td>
<td>(Jeon et al., 2002)</td>
<td>99</td>
<td></td>
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<tr>
<td>Potassium permanganate</td>
<td>Alginate acid</td>
<td>(Manohar et al., 2002)</td>
<td>642.32</td>
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<tr>
<td>2-mercaptobenzimidazole</td>
<td>Clay</td>
<td>(Dornia et al., 2006)</td>
<td>140</td>
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<tr>
<td>Fe_{2}O_{3}</td>
<td>GMA chelating resin</td>
<td></td>
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<td></td>
</tr>
<tr>
<td>NaOH, Na_{2}S and SDS</td>
<td>Chicken feathers</td>
<td>(Al-Asheh et al., 2003)</td>
<td>0.39</td>
<td>0.23</td>
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<tr>
<td>Iron oxide (Fe(NO_{3})<em>{3}.9H</em>{2}O)</td>
<td>Sand</td>
<td>(Lai and Chen, 2001)</td>
<td>0.259</td>
<td>1.2</td>
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<tr>
<td>Citric acid</td>
<td>Corn cobs</td>
<td>(Vaughan et al., 2001)</td>
<td>0.67</td>
<td>0.62</td>
<td>0.6</td>
<td>0.44</td>
<td>0.59</td>
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<tr>
<td>Phosphoric acid</td>
<td>Corn cobs</td>
<td>(Dornia et al., 2006)</td>
<td>0.99</td>
<td>0.37</td>
<td>0.4</td>
<td>0.40</td>
<td>0.46</td>
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<tr>
<td>HCl</td>
<td>Oak sawdust</td>
<td>(Argun et al., 2007)</td>
<td>3.2</td>
<td>3.3</td>
<td>1.7</td>
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Table 3. Adsorption capacities (mg/g) of various adsorbents modified with biological methods for heavy metals

<table>
<thead>
<tr>
<th>Modification Agents</th>
<th>Adsorbent</th>
<th>Sources</th>
<th>Cu^{2+}</th>
<th>Co^{2+}</th>
<th>Zn^{2+}</th>
<th>Cd^{2+}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chryseomonas luteola</td>
<td>Calcium and sodium alginate</td>
<td>(Ozdemir et al., 2005)</td>
<td>55.25</td>
<td>64.10</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Pine bark and swage sludge</td>
<td>(Gibert et al., 2005)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Composting microorganisms</td>
<td></td>
<td></td>
<td>3.9</td>
<td>12.1</td>
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</tr>
</tbody>
</table>

Conclusions

Different types of modification agents, adsorbents heavy metals have been reviewed in this study. It was observed that chemical modification especially polymerization, oxidation and acidic treatment have generally been used for modification. Physical and physiochemical activation have frequently been used for activated carbon production or improve of it’s capacity. Biological modifications of adsorbent were rather rare and scarce. The modification techniques have been reported to increase of adsorption in general. Probable effect of modification agents on the adsorbent have summarized as increase of porosity, increase of functional groups, change of surface charge for electrostatic interaction and chelat formation.

References


Petrogenesis of Skenderbeu Peridotites (Western Ophiolitic Belt, Albania)

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1Geological Survey of Albania, Blloku ‘Vasil Shanto’, Tirana, Albania; 2Polytechnic University of Tirana, Faculty of Geology and Mines, Rruga Elbasani, Tirana, Albania

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Abstract: This paper presents results of a study on the field relations, petrographic features, mineral and rock chemistry and petrology of peridotites from the Skenderbeu massif, which belongs to western belt of Jurassic Albanian ophiolites. As confirmed by petrological characteristics, the geological section of the Skenderbeu massif consists, from the bottom to the top, of a mostly harzburgite and diopside harzburgite tectonite sequence, plagioclase lherzolite transitional zone, magmatic gabbros and troctolites and basalts. Based on the bulk chemistry, mineral chemistry and modal composition, the peridotites of Skenderbeu massif have undergone a relatively low partial melting grade which increases from the centre of the massif towards its western sectors. The low partial melting grade was also supported by the very limited abundance of the dunites and chromite ore bodies which, in turn, are higher in Al. Both high-temperature asthenospheric fabrics and high-stress and relatively low temperatures lithospheric fabrics are present in the peridotites of the Skenderbeu massif.

Key Words: Ophiolite, Skenderbeu massif, ultramafic, tectonite, cumulate

Introduction

The ultramafic massif of Skenderbeu, which belongs to the western ophiolitic belt of Albania (Figure 1), consists of a thick (3.5 km) rock sequence. Its generalized geological profile, from the bottom to the top, is composed from the follows rock sequences (Shenjatari & Jaurri, 2001): tectonite sequence composed of lherzolite, clinopyroxene (diopside) harzburgite and dunite; transitional zone composed mainly of plagioclase lherzolite; magmatic sequence composed of troctolite, gabbro and, finally, a volcanic sequence composed of basalts. Because this massif is scarce in chromium it has not been between the most studied ultrabasic massifs of Albanian ophiolites and, as a consequence, the petrological data on it are scarce. The first structural model of the Skanderbeu massif was firstly given by Meshi et al., 2009), based on the foliation and lineation measurements. Onuzi et al (2007) presented a petrological model based on a more completed geochemical database.

The geological observations and microscopic studies of the first author and geochemical data from other studies (Onuzi et al., 2007) in which the first author was involved, are used in order to light some petrogenetic aspects of the Skenderbeu ultramafic massif. The harzburgites and lherzolites contain metamorphic textures derived during the diapiric uplift of the massif. The lherzolite and clinopyroxene (diopside) harzburgite could represent a weakly depleted upper mantle (Nicolas and Dupuy, 1984) while the harzburgites and dunites are the most refractory residual rocks of the massif. On the other hand, plagioclase lherzolites were probably resulted from a plagioclase-clinopyroxene magmatic impregnation into formerly depleted harzburgites (Nicolas e Prinzhofe,1983; Benn et al., 1988; Cannat etj, 1990; Tartarotti e Vaggelli,1994). Finally, the lack of metallurgical chromium deposits along with the Al-rich accessory chromite, that contrast the high chromium potential and Cr-rich chromite of the Bulqiza ultramafic massif (Beqiraj, 2008), shows that Skenderbeu mantle section suffered a lower partial melting grade with respect to Bulqiza one. The presence of the clinopyroxene harzburgites and lherzolites, the scarce extent of dunites and harzburgites in this massif, the geochemical features of minerals and rocks and, finally, the scarce abundance of chromite ore bodies, which are mostly higher in Al, all favour the opinion that peridotites of the Skenderbeu massif suffered a lower partial melting grade with respect to Bulqiza analogues (Beqiraj, 2008, Beqiraj and Masi, 2009).

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Geological setting and sampling

The Skenderbeu massif that belongs to the Western belt of Albanian ophiolites covers more than 112 Km² in central Albania (Figure 1). It is overthrust westward on the T3-J1 limestone and on the younger (Pg1-2) flysch formations. The early J1-Cr1 flysch or melange formations rest transgressively and/or tectonically on the massif. Finally, the mollasic formations of Burreli depression, that represent the youngest sedimentary cover, rest transgressively on the massif. As shown in Fig. 2, that gives a generalized stratigraphic log of the massif, its geological section, from the bottom to the top, consists of a thick tectonite section, a thin plutonic section and, finally, a reduced basaltic sequence. The thicker tectonite sequence is composed of lherzolite, clinopyroxene harzburgites, harzburgites and dunites. Lherzolites and diopside harzburgites, that represent the less depleted mantle section of the massif, crop out in the central sectors of the massif, while the harzburgites spread out in the western part. The cumulate sequence consists of troctolite and gabbros, whereas on the top of the massif section occurs a reduced volcanic section mostly composed of basalts. The plagioclase lherzolites with small and scarce dunite lenses that lay between the two above sequences represent the transitional zone, as usually observed in other ophiolitic complexes (Beqiraj, 2008). This unit may represent the lowermost part of the cumulate sequence (Pallister and Hopson, 1981; Elthon et al., 1982; Shallo et al., 1989) or it is residual (Nicolas and Prinzhofer, 1983; Benn et al., 1988; Tashko and Marto, 1990). Scarcie pyroxenite and microgabbro dykes are present in the uppermost part of tectonite sequence and plagioclase lherzolites.

A representative number of almost all lithotypes was collected from the tectonite sequence, through two East-West extended profiles (Fig. 1). 9 samples of massif lithotypes were analysed for both mineral and whole-rock chemical composition at the Department of Geological Sciences, University of Vienna.

**Figure 1.** Schematic Geological Map of the ultramafic massif of Skenderbeu
Analytical procedure

All the samples were studied for petrography in thin section by optical microscope, while the electron microprobe analyses were carried out on polished thin sections coated with carbon, at 15 kV accelerating voltage, 40 nA beam current intensity and 5 μm electron beam diameter, with a Jeol XA 8600 (Salzburg University) equipped with four wavelength dispersive spectrometers (WDS) and a Si (Li) energy-dispersive spectrometer (EDS). Major and trace elements were analysed by X-ray fluorescence (XRF) using a Philips PW 2400 at the Department of Geological Sciences, University of Vienna (according the procedure described by Hoeck et al., 2002).

Results and Discussion

The dunite, that represent the most refractory rock type of the upper part of the mantle sequence is very scarce in the Skanderbeu massif. The most abundant ultramafic rocks are harzburgites (olivine+orthopyroxene+chromite) followed by diopside-bearing harzburgites (olivine + orthopyroxene + clinopyroxene (3-5%) + chromite and lherzolites (olivine+orthopyroxene + clinopyroxene (>5%) + chromite) (Fig. 3). Olivine crystals in harzburgite range in size from 0.1 mm to a 6,0 mm and display both uniform and undulose extinction. The olivine from harzburgite displays shape preferred orientation formed either by ribbons of olivine porphyroclasts that are parallel to the foliation and define it in thin section or by imbricate elongate neoblasts. Orthopyroxenes grain size varies from approximately 0,5 mm to greater than 4 mm in thin section. Orthopyroxene grains show a
variety of crystal morphology from interlobate to polygonal and they are commonly kinked or slightly bent and display clinopyroxene exsolution lamellae. In the samples with inequigranular textures the large orthopyroxene grains contain olivine inclusions. Chromite ranges in size from 0,1 mm to 1,0 mm and may be equant (subhedral to euhedral) or elongate. Chromite lineations, that is common observed, can be formed by an alignment of equant crystals or may be formed by anhedral elongate grains. Clinopyroxene is commonly observed as interstitial anhedral grains. Its crystals generally have exsolution lamellae and well developed cleavage that is often slightly bent.

Figure 3. Photomicrographs of the main lithotypes (a = Diopside harzburgite; b = Milonitized harzburgite; c=dunite; d = Plagioclase lherzolite; Ol – olivine; Opx – orthopyroxene, Cpx – clinopyroxene; Pl – plagioclase; Sp – spinel.

Foliation and lineation, as macroscopically distinguishable penetrative structure, are often observed in the harzburgites, diopside harzburgites and lherzolites. These finite strain markers result from plastic flow, which causes shape and lattice fabric development representing a kinematic record (Nicolas and Poirier 1976). The mantle rocks contain metamorphic textures derived during the diapiric uplift of the massif. The low-T, high-P millonitic textures are found along the contact of the massif with limestones, while the high-T, high-P porphyroclastic and granoblastic textures are observed in the central sectors of the massif, respectively. Based on foliation by pyroxene, a symmetric anticline form can be inferred for the massif (Fig. 4), whereas the stereogram of lineation shows a north-western inclination of the massif (Fig. 5). With respect to modal variations, a gradual disappearance of mineral phases (ol+sp+opx+cpx - ol+sp+opx - ol+sp), from the bottom to the top of the tectonite sequence, was observed (Fig. 6). Such a modal variation correlates with the upward increase of partial melting (Dick et. al. 1984) that resulted in a gradual melt extraction from the mantle residual. The peridotite in the Skenderbeu massif, like other ophiolites, has been subject to alteration by serpentinitization, on a regional scale, either by on-axis processes active during spreading (Coulton et al., 1995) or by processes that were active during emplacement and weathering (Coleman, 1977).
As shown by table 1, there is a apparent major element variation among the various petrographic mantle types. Al, Ca and Na increase from dunite, through harzburgite to diopside harzburgite and lherzolite, the highest values being encountered in plagioclase lherzolite, due to the impregnated clinopyroxene and plagioclase. The harzburgite tectonite has the characteristics of refractory residuum resulting from the extraction of a basaltic melt produced by partial melting of a lherzolite.

Table 1. Bulk composition of the ultramafic rocks from Skenderbeu massif (Oxides are given in wt%) (data from Onuzi et al, 2005-2007)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Rock type</th>
<th>SiO$_2$</th>
<th>TiO$_2$</th>
<th>Al$_2$O$_3$</th>
<th>Fe$_2$O$_3$</th>
<th>MnO</th>
<th>MgO</th>
<th>Na$_2$O</th>
<th>K$_2$O</th>
<th>P$_2$O$_5$</th>
<th>Summe</th>
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<tbody>
<tr>
<td>SK540</td>
<td>Harzburgite</td>
<td>41.53626</td>
<td>0.01664</td>
<td>0.785796</td>
<td>7.968897</td>
<td>0.120181</td>
<td>39.36376</td>
<td>1.303497</td>
<td>0.065637</td>
<td>0.012843</td>
<td>98.635</td>
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<td>SK541</td>
<td>Harzburgite</td>
<td>44.66</td>
<td>0.019</td>
<td>0.79</td>
<td>8.78</td>
<td>0.13</td>
<td>43.06</td>
<td>1.47</td>
<td>0.01</td>
<td>0.008</td>
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<td>Harzburgite</td>
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<td>0.026</td>
<td>0.92</td>
<td>8.99</td>
<td>0.12</td>
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<td>0.69</td>
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<td>Dunite</td>
<td>38.82251</td>
<td>0.01338</td>
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<td>10.31253</td>
<td>0.124247</td>
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<td>SK550</td>
<td>Lherzolite</td>
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<td>0.041387</td>
<td>2.389169</td>
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<td>SK556</td>
<td>Pr-Lherzolite</td>
<td>39.93491</td>
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<td>2.804411</td>
<td>0.086947</td>
<td>0.015321</td>
<td>99.317</td>
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</table>

Table 2. Composition of olivine (Oxides are given in wt%) (data from Onuzi et al, 2005-2007)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Rock type</th>
<th>SiO$_2$</th>
<th>TiO$_2$</th>
<th>Al$_2$O$_3$</th>
<th>Cr$_2$O$_3$</th>
<th>FeO</th>
<th>MnO</th>
<th>NiO</th>
<th>MgO</th>
<th>CaO</th>
<th>Na$_2$O</th>
<th>K$_2$O</th>
<th>Summe</th>
<th>XMg</th>
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<tbody>
<tr>
<td>SK551</td>
<td>Pl-lherzolite</td>
<td>40.85</td>
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<td>0.03</td>
<td>8.48</td>
<td>0.14</td>
<td>0.40</td>
<td>50.43</td>
<td>0.03</td>
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<td>100.37</td>
<td>0.91</td>
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</tr>
<tr>
<td>SK541</td>
<td>Harzburgite</td>
<td>40.97</td>
<td>0.00</td>
<td>0.01</td>
<td>0.01</td>
<td>8.51</td>
<td>0.14</td>
<td>0.41</td>
<td>50.74</td>
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<td>101.08</td>
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<tr>
<td>SK550</td>
<td>Pl-lherzolite</td>
<td>40.73</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
<td>9.27</td>
<td>0.14</td>
<td>0.44</td>
<td>50.11</td>
<td>0.02</td>
<td>0.00</td>
<td>100.84</td>
<td>0.90</td>
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</tr>
<tr>
<td>SK543</td>
<td>Dunite</td>
<td>40.51</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
<td>9.24</td>
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<td>0.33</td>
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<tr>
<td>SK542</td>
<td>Harzburgite</td>
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<td>0.01</td>
<td>0.03</td>
<td>8.46</td>
<td>0.11</td>
<td>0.41</td>
<td>50.61</td>
<td>0.02</td>
<td>0.00</td>
<td>100.47</td>
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</table>

Table 3. Composition of accessory chromite (Oxides are given in wt%) (data from Onuzi et al, 2005-2007)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Rock type</th>
<th>SiO$_2$</th>
<th>TiO$_2$</th>
<th>Al$_2$O$_3$</th>
<th>Cr$_2$O$_3$</th>
<th>FeO</th>
<th>MnO</th>
<th>NiO</th>
<th>MgO</th>
<th>CaO</th>
<th>Na$_2$O</th>
<th>K$_2$O</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>SK551</td>
<td>Pl-lherzolite</td>
<td>0.026</td>
<td>0.04</td>
<td>51.91</td>
<td>14.556</td>
<td>12.694</td>
<td>0.102</td>
<td>0.271</td>
<td>18.868</td>
<td>98.469</td>
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<td></td>
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</tr>
<tr>
<td>SK550</td>
<td>Pl-lherzolite</td>
<td>0.133</td>
<td>0.02</td>
<td>52.01</td>
<td>13.846</td>
<td>14.196</td>
<td>0.118</td>
<td>0.263</td>
<td>17.891</td>
<td>98.466</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>SK543</td>
<td>Dunite</td>
<td>0.022</td>
<td>0.08</td>
<td>38.03</td>
<td>26.525</td>
<td>17.985</td>
<td>0.155</td>
<td>0.204</td>
<td>15.434</td>
<td>98.430</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>SK542</td>
<td>Harzburgite</td>
<td>0.022</td>
<td>0.09</td>
<td>38.26</td>
<td>27.836</td>
<td>16.256</td>
<td>0.158</td>
<td>0.155</td>
<td>15.687</td>
<td>98.455</td>
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<td>SK731</td>
<td>Harzburgite</td>
<td>0.475</td>
<td>0.06</td>
<td>42.11</td>
<td>26.768</td>
<td>14.100</td>
<td>0.042</td>
<td>0.180</td>
<td>17.165</td>
<td>100.895</td>
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<td>0.03</td>
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<td>35.750</td>
<td>17.170</td>
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<td>14.266</td>
<td>98.786</td>
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</tr>
<tr>
<td>SK734</td>
<td>Lherzolite</td>
<td>0.030</td>
<td>0.14</td>
<td>38.62</td>
<td>30.268</td>
<td>15.647</td>
<td>0.050</td>
<td>0.193</td>
<td>15.974</td>
<td>100.929</td>
<td></td>
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</tr>
<tr>
<td>SK733</td>
<td>Lherzolite</td>
<td>0.011</td>
<td>0.08</td>
<td>43.45</td>
<td>24.911</td>
<td>15.662</td>
<td>0.051</td>
<td>0.203</td>
<td>16.437</td>
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<tr>
<td>SK730</td>
<td>Lherzolite</td>
<td>0.000</td>
<td>0.00</td>
<td>22.40</td>
<td>13.925</td>
<td>0.057</td>
<td>0.255</td>
<td>0.000</td>
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<td>54.414</td>
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<tr>
<td>SK27</td>
<td>Harzburgite</td>
<td>0.019</td>
<td>0.13</td>
<td>30.02</td>
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<td>0.122</td>
<td>14.037</td>
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</tr>
</tbody>
</table>
### Table 4. Composition of orthopyroxene (Oxides are given in wt%, cations as a.f.u) (data from Onuzi et al, 2005-2007)

<table>
<thead>
<tr>
<th>No</th>
<th>SK-541</th>
<th>SK550</th>
<th>SK731</th>
<th>SK734</th>
<th>SK730</th>
<th>SK733</th>
<th>SK727</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>56.34</td>
<td>55.90</td>
<td>56.37</td>
<td>57.33</td>
<td>56.67</td>
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<td>TiO₂</td>
<td>0.02</td>
<td>0.028</td>
<td>0.031</td>
<td>0.033</td>
<td>0.022</td>
<td>0.022</td>
<td>0.024</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>2.09</td>
<td>3.101</td>
<td>3.22</td>
<td>1.53</td>
<td>2.46</td>
<td>2.89</td>
<td>1.55</td>
</tr>
<tr>
<td>Cr₂O₃</td>
<td>0.43</td>
<td>0.286</td>
<td>0.58</td>
<td>0.23</td>
<td>0.32</td>
<td>0.435</td>
<td>0.25</td>
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<tr>
<td>FeO</td>
<td>5.74</td>
<td>6.69</td>
<td>5.59</td>
<td>5.98</td>
<td>6.24</td>
<td>6.23</td>
<td>5.76</td>
</tr>
<tr>
<td>MnO</td>
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<td>0.144</td>
<td>0.134</td>
<td>0.145</td>
<td>0.15</td>
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<td>NiO</td>
<td>0.103</td>
<td>0.069</td>
<td>0.068</td>
<td>0.087</td>
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<td>0.04</td>
</tr>
<tr>
<td>MgO</td>
<td>34.80</td>
<td>33.88</td>
<td>35.12</td>
<td>35.63</td>
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<td>35.61</td>
</tr>
<tr>
<td>CaO</td>
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<td>0.268</td>
<td>0.44</td>
<td>0.70</td>
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<td>Na₂O</td>
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<td>0.015</td>
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<td>0.00</td>
<td>0.01</td>
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<tr>
<td>K₂O</td>
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<td>0.001</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
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</tr>
<tr>
<td>BaO</td>
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<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Total</td>
<td>100.64</td>
<td>100.69</td>
<td>101.42</td>
<td>101.23</td>
<td>101.42</td>
<td>101.43</td>
<td>100.97</td>
</tr>
</tbody>
</table>

### Table 5. Composition of clinopyroxene (Oxides are given in wt%, cations as a.f.u) (data from Onuzi et al, 2005-2007)

<table>
<thead>
<tr>
<th>No</th>
<th>SK-541</th>
<th>SK550</th>
<th>SK731</th>
<th>SK734</th>
<th>SK730</th>
<th>SK733</th>
<th>SK727</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>53.982</td>
<td>53.918</td>
<td>53.30</td>
<td>52.63</td>
<td>52.28</td>
<td>53.25</td>
<td>53.34</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.04</td>
<td>0.11</td>
<td>0.11</td>
<td>0.22</td>
<td>0.17</td>
<td>0.155</td>
<td>0.11</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>1.528</td>
<td>2.60</td>
<td>2.89</td>
<td>3.04</td>
<td>3.53</td>
<td>2.55</td>
<td>2.23</td>
</tr>
<tr>
<td>Cr₂O₃</td>
<td>0.298</td>
<td>0.41</td>
<td>0.63</td>
<td>0.76</td>
<td>0.86</td>
<td>0.45</td>
<td>0.63</td>
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<tr>
<td>FeO</td>
<td>1.933</td>
<td>2.60</td>
<td>2.05</td>
<td>1.93</td>
<td>2.22</td>
<td>2.20</td>
<td>1.99</td>
</tr>
<tr>
<td>MnO</td>
<td>0.091</td>
<td>0.09</td>
<td>0.08</td>
<td>0.065</td>
<td>0.07</td>
<td>0.08</td>
<td>0.075</td>
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<tr>
<td>NiO</td>
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<td>0.064</td>
<td>0.029</td>
<td>0.043</td>
<td>0.036</td>
<td>0.038</td>
<td>0.02</td>
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<tr>
<td>MgO</td>
<td>18.347</td>
<td>17.765</td>
<td>17.73</td>
<td>17.33</td>
<td>18.00</td>
<td>17.81</td>
<td>17.87</td>
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<tr>
<td>CaO</td>
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<td>23.13</td>
<td>24.54</td>
<td>24.52</td>
<td>24.20</td>
<td>24.14</td>
<td>24.40</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.04</td>
<td>0.40</td>
<td>0.087</td>
<td>0.13</td>
<td>0.06</td>
<td>0.091</td>
<td>0.08</td>
</tr>
<tr>
<td>K₂O</td>
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<td>0</td>
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<td>0</td>
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<tr>
<td>BaO</td>
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<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Total</td>
<td>100.532</td>
<td>101.11</td>
<td>101.45</td>
<td>100.67</td>
<td>101.42</td>
<td>100.76</td>
<td>100.74</td>
</tr>
</tbody>
</table>

| Si   | 1.95  | 1.93  | 1.90  | 1.90  | 1.93  | 1.92  | 1.92  |
| Al³⁺| 0.05  | 0.06  | 0.08  | 0.095 | 0.07  | 0.077 | 0.07  |
| Al⁶⁺| 0.01  | 0.04  | 0.035 | 0.034 | 0.026 | 0.031 | 0.03  |
| Ti   | 0.001 | 0.03  | 0.003 | 0.006 | 0.003 | 0.004 | 0.003 |
| Cr   | 0.008 | 0.012 | 0.018 | 0.021 | 0.012 | 0.013 | 0.018 |
| Fe³⁺| 0.003 | 0.004 | 0.003 | 0.003 | 0.003 | 0.003 | 0.003 |
| Fe⁶⁺| 0.055 | 0.074 | 0.06  | 0.055 | 0.063 | 0.063 | 0.057 |
| Mn   | 0.003 | 0.003 | 0.002 | 0.002 | 0.002 | 0.003 | 0.002 |
| Ni   | 0.002 | 0.002 | 0.001 | 0.001 | 0.001 | 0.001 | 0.001 |
| Mg   | 0.98  | 0.95  | 0.94  | 0.93  | 0.96  | 0.96  | 0.96  |
| Ca   | 0.93  | 0.89  | 0.94  | 0.95  | 0.93  | 0.93  | 0.94  |
| Na   | 0.003 | 0.03  | 0.006 | 0.009 | 0.005 | 0.006 | 0.005 |
| K    | 0     | 0.001 | 0     | 0     | 0     | 0     | 0     |
| Sum  | 4.014 | 4.014 | 4.01  | 4.01  | 4.014 | 4.016 | 4.017 |
The Skenderbeu massif is very scarce in chromium deposits and, on the other hand, the ore body chromite is higher in Al (Table 6), thus showing that the mantle rocks of this massif suffered a relatively low partial melting.

**Table 6.** Composition of chromite ore bodies

<table>
<thead>
<tr>
<th>No.</th>
<th>SiO₂</th>
<th>MgO</th>
<th>CaO</th>
<th>Cr₂O₃</th>
<th>Al₂O₃</th>
<th>TiO₂</th>
<th>FeO</th>
<th>Fe₂O₃</th>
<th>MnO</th>
<th>CoO</th>
<th>NiO</th>
<th>V₂O₅</th>
<th>P₂O₅</th>
<th>Na₂O</th>
<th>K₂O</th>
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</thead>
<tbody>
<tr>
<td>82/2</td>
<td>2.20</td>
<td>16.4</td>
<td>0.1</td>
<td>34.4</td>
<td>29.3</td>
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<td>11.4</td>
<td>2.3</td>
<td>0.2</td>
<td>0.2</td>
<td>0.1</td>
<td>0.2</td>
<td>0.1</td>
<td>0.56</td>
<td>0.12</td>
</tr>
<tr>
<td>202</td>
<td>2.79</td>
<td>17.3</td>
<td>0.1</td>
<td>33.4</td>
<td>30.0</td>
<td>0.21</td>
<td>7.1</td>
<td>6.0</td>
<td>0.2</td>
<td>0.2</td>
<td>0.1</td>
<td>0.2</td>
<td>0.1</td>
<td>0.62</td>
<td>0.12</td>
</tr>
</tbody>
</table>

**Figure 6.** Modal variation of the of Olivine, Orthopyroxene and Clinopyroxene in the Peridotites of Skenderbeu massif.

**Figure 7.** Triangle diagram of the Pyroxene composition.
Petrogenetic implications

Peridotites of Skenderbeu massif contain penetrative structures, foliation and lineation, which result from plastic flow (Nicolas and Poirier 1976) showing a north-western inclination of a symmetric anticline of the massif. The high-temperature asthenospheric deformation fabrics are characteristic for the lower herzolites and harzburgites while all the peridotites are affected by intense shear deformation developed in lithospheric conditions. The upper plagioclase peridotites of the Skenderbeu massif, as most of the western ultramafic massifs, are interpreted as non primary mantle lherzolites, but an artifact of extreme deformation of dunites and harzburgites impregnated by basaltic liquids and intruded by gabbroic veins and sills (Meshi et al., 2009). The coarse-grained textures of harzburgites and dunites and porphyroclastic to submylonitic textures of plagioclase peridotites record asthenospheric deformation conditions at high temperatures (between 1000 and 1200°C) and high-stress and relatively low temperatures lithospheric conditions (800 to 1000°C), respectively (Meshi et al., 2009).

The peridotites of the Skenderbeu massif have contents of magmatophile elements (Ca, Al, Na) similar with that of Ronda (Frey et al., 1985; Gervilla, 1993), Lanzo (Bodinier et al., 1987) and Liguria (Beccaluva et al., 1984; Ottonello et al., 1984), thus being more fertile than the extremely refractory analogues rocks from Bulqiza (Beqiraj, 2008, 2009), New Caledonia (Prinzhofer & Allegre, 1985), Troodos and Vourinos (Beccaluva et al., 1984). Based on the contents of the above elements three rock types are distinguished: i) the most depleted harzburgites of the western part of the massif, ii) clinopyroxene – harzburgites and lherzolites of the central part and, finally, plagioclase lherzolites of the transitional zone with impregnated clinopyroxene and plagioclase. The observed gradual disappearance of mineral phases (ol+sp+opx+cpx - ol+sp+opx - ol+sp), from the bottom to the top of the tectonite sequence, meet with the increasing of the partial melting grade in this direction. In the Fig. 8, where the composition of Skenderbeu peridotites is confronted with that of peridotites from other geodynamic settings, is shown that the peridotites from Skenderbeu massif have high (>1.5%) content of Al₂O₃ in orthopyroxene and low (<0.5) values of Cr/(Cr+Al), thus being similar with peridotites from the passive oceanic margins (Bonatti & Michael, 1989).

![Diagram of Al₂O₃ (in Orthopyroxene) versus Cr/(Cr+Al) report (in Chromite) Fields of passive oceanic and subduction margins according to Bonatti & Michael, 1989.](image)

Figure 8. Diagram of Al₂O₃ (in Orthopyroxene) versus Cr/(Cr+Al) report (in Chromite) Fields of passive oceanic and subduction margins according to Bonatti & Michael, 1989.

The chromite from Skenderbeu peridotites shows lower values (<0.6) of the Cr/(Cr+Al) report and higher (0.16-0.89%) content of TiO₂ than the chromite from eastern analogues. Low Cr (high Al) chromites are probably precipitated from tholeiitic melts (Allan et. al. 1988; Kamenetsky et. al., 2001), favoring the opinion that the Skenderbeu peridotites are generated in a MORB-type geodynamic setting (Dick et. al. 1984; Allan et. al. 1988) (Figure. 9).
The bulk chemistry and mineral chemistry along with the lack or scarce abundance of dunites and Al-rich chromitites favor the opinion that the Skanderbeu massif belongs to the western lherzolite-harzburgite ophiolite belt that have suffered a relatively low partial melting grade.

![Graph](image)

**Figure 9.** TiO2 versus Al2O3 in Chromite from Skenderbeu peridotites (SSZ- and MORB-type peridotite fields according to Allan *et al.*, 1988).

**Conclusions**

The Skenderbeu massif is a typically lherzolite-harzburgite massif of the western belt of the Albanian ophiolite complex. In contrast with eastern harzburgite-type ultrabasic massifs it is characterized by the lack or scarce abundance of dunites and Al-rich chromitites.

A gradual disappearance of mineral phases (ol+sp+opx+cpx - ol+sp+opx - ol+sp), from the bottom to the top of the tectonite sequence, was observed, which correlates with the upward increase of partial melting that resulted in a gradual melt extraction from the mantle residual.

Based on foliation and lineation, a symmetric anticline form can be inferred for the massif showing a north-western inclination. All the peridotites are affected by intense lithospheric shear deformation, while the lower lherzolites and harzburgites contain high-temperature asthenospheric deformation fabrics.

Both bulk and mineral chemistry show that peridotites of the Skanderbeu massif represent a mantle residual remained after the extraction of a basaltic melt during a relatively low partial melting of the mantle lherzolite.

The composition of orthopyroxene and chromite show that Skenderbeu peridotites are similar with those of passive oceanic margins favoring the opinion that they are generated in a MORB-type geodynamic setting.

**Acknowledgement:** We acknowledge Prof. Dr. Friedrich Koller, Prof. Dr. Volker Höck for the microprobe analyses and Prof. As. Dr. Kujtim Onuzi for the availability he always showed.

**References**


Coleman RG., 1977. Ophiolites: Ancient Oceanic Lithosphere, 229 pp. Springer Verlag, 236 Gray's Inn Road, Floor 6, London WC1X 8HB, United Kingdom.


Analysis of Seismic Noise

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Abstract: To select a potential location for a future seismological station properly, it is of crucial importance to explore the existing local seismic tremor recorded by seismographs. This tremor/noise is referred to as seismic tremor, where it is necessary to define as precisely as possible its spectral characteristics. On the other hand, for the needs of micro zoning, it is important to define the existence of possible geological layers and structures immediately below the location or farther, whose resonant characteristics could intensify the ground motion under the effect of strong (according to magnitude) local or regional earthquakes. Such local effects could aggravate and, in some cases, make impossible the accurate definition of the earthquake energy (their magnitude) and the parameters of concern for the seismological and engineering-seismological investigations. Therefore, in addition to other geophysical methods, it is of particular importance to define the spectral characteristics of the local tremor at the investigated sites.

Key words: analysis, seismic, investigations, noise, frequency.

Characteristics of Seismic Tremor

Generally, the two frequency ranges of the spectral content of the seismic noise (hereinafter referred to as tremor) are of seismological importance. These are the short-periodic and the long-periodic tremor. Since their nature and sources are different, a different approach to measuring of these tremors and interpretation of the obtained results from the measurements is imposed. In these measurements, corresponding and statistically consistent ground velocity power density spectra are to be obtained. The limits of the frequencies within which measurements will be made are also to be selected: up to 0.1 Hz in the low-frequency (long-periodic) part of the spectrum and up to 10 Hz in the high-frequency (short-periodic) range of the tremor spectrum. The following are the frequencies at which individual geological layers below the location would be in resonance conditions:

It should be mentioned however that there is also the effect of the so called artificial tremor that could interfere with the real seismic tremor at the site. The artificial tremor is generated by the motion of vehicles, industrial activities and motion of persons in the immediate vicinity of the site and also the motion of the persons that perform the measurements. These effects are in the frequency interval of 10 to 30 Hz. Practically, these are beyond the frequencies of interest, but if their effect is too strong, the frequencies of interest will be contaminated due to the limitations of the procedures that are used in spectral analyses. In recording a contaminated tremor, the motion (motion of pedestrians or traffic) is mostly presented as a set of strong vibrations, while the industrial tremor is mostly stationary and occurs in the form of peaks. One of the greatest problems in measuring the seismic tremor is the wind effect. Unfortunately, the wind can generate such a noise whose spectrum can overlap with the spectrum of the seismic tremor which is of concern. The seismological practice has seen that natural seismic tremor is generally non-stationary, with frequencies ranging from 0.2 to 0.5 Hz. It changes with the passing of time and depends on the regional climatic/weather changes, i.e., conditions, with amplitudes that could be increased even ten times within a short period of time. In conclusion, it can be stated that the investigations of the characteristics of tremors are mainly based on the assumption that the natural tremor of a certain location could have the same or similar spectral characteristics as in the case of an earthquake effect. The main assumption is that the occurrence of certain spectral peaks in the spectrum of the measured tremors, their frequency and amplitude could result from the existence of certain geological layers below the site. The existence of such resonant spectral peaks, i.e., frequencies, which on the other hand, point out the possibility for local amplification of ground motion during earthquakes, is of direct importance also for the investigation of the seismic risk both at

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the location itself and its immediate surrounding. Special attention should be paid to the validity of the obtained results that depends on the selected measuring equipment, the instrumental noise and the effect of external excitations, i.e., the sources producing an artificial seismic noise that has an effect upon the measuring of the real seismic tremor. Considering the above stated, it is clear that conditions assuming sufficiently calm (in the seismological sense) locations can hardly be fulfilled. This imposes careful measurement of the seismic tremors and precise definition of their spectral content in order to fulfil the conditions for operation of the seismological station later during the installation of the seismological equipment and the selection of optimal filters. The sensitivity of the seismological station, i.e., the installed digital seismograph should be sufficiently high in order to record the seismic tremor clearly and make it visible on the seismograms.

**Measurement of Tremors**

To measure the tremors, it is necessary to have a corresponding equipment and software support for processing of the obtained data. The equipment used for these measurements represented field and laboratory equipment. The field equipment consisted of the following:

1. Digital seismograph composed of:
2. Seismometers (SS1-Ranger, Kinematics Inc.);
3. Digital recorder (SSR-1, Kinematics Inc.);
4. Portable computer necessary for immediate control of the digital recorder and archiving of data (HP Laptop + SW software, Kinematics Inc.).

The laboratory processing was done by use of a powerful computer with a corresponding software (Mat lab based, TSOFT, Dadisp 2002 and own software) necessary for the processing of the seismological data. Seismometers are necessary for such investigations. Considering the requirement regarding their sensitivity and resolution, geophones are not recommended to be used. Still, geophones were also used in these measurements for the purpose of comparing the obtained results. The most important requirement that should be fulfilled is that the instrumental noise of the seismometers be much lower than the level of the natural seismic noise at the location.

**Results obtained from measurements of seismic tremor**

**Seismological Station Prizren**

The geological characteristics of the selected location in the surrounding of the city of Prizren are given in the excerpt from the geological map for this area. The measurements were performed in calm weather conditions (without wind). A number of recordings were made: functional tests on equipment and seismometers and recordings of tremors.

**Characteristics of Uncorrected Time Records and Their Spectra**

The location is situated in a rocky part, with a hardly accessible road (compacted earth and stone) in its vicinity. There are no nearby houses, but motion of pedestrians is frequent (picnickers and other). The two seismometers were at a distance of 3 – 4 m, whereas SS1_2238 was placed on rock, while SS1_2251 was placed on a somewhat “softer” base, hard and rocky. Figure 1 and Figure 2 clearly show that the level of seismic tremor recorded on channel 1 (seismometer SS1_2238) is almost the same as that recorded on channel 2 (seismometer SS1_2251). Note worthy is also the very similar spectral content of the records on both channels. Comparing the spectrogram’s of the records (Figures 3, 4 & 5,6), it can generally be stated that the situation is very similar, with weak component at 50 Hz, which is somewhat more expressive on the first channel. The contribution of the individual spectral components is up to 50 Hz for the SS1_2238 record and up to 60 Hz for the SS1_2251 record. The characteristic peaks on the PSD spectra are almost on the same place for frequencies higher than 0.2 Hz as follows:

Characteristic spectral peaks (Hz):
- Channel 1: 0.3, 0.5 (sharp peak), 2.5 (large peak), 10.0 (small set), 50 pronounced noise that is due to contamination from the network power supply in the surrounding.
- Channel 2: starts at 0.04; with peaks at 0.28, 0.35, 0.2, 8.0, 10.0, and 50 (slightly expressed).
Characteristics of Corrected Time Records and Their Spectra

To avoid the effects of the sets of noises that take place as a result of the local disturbances during the measurements, three segments of the size of 8192 terms were selected per each measurement. The time difference between two adjacent quantities in the digital records is 0.005 seconds, which corresponds to the already mentioned sampling frequency of 200 Hz. In that way, in each of the segments with duration of 40.96 sec., there is an exact 213 number of terms by which the occurrence of the numerical noise is avoided in the Fourier spectral analysis (by adding or subtracting of terms in order that the number be integer amount of 2K). The signals were corrected via the amplitude spectrum of the response functions obtained for each seismometer. The PSD power spectra that are common for each of the segments, for ultimate frequency of up to 50 Hz, are presented further in the text. There are no sets of peaks and the signal shape is almost uniform on the uncorrected time record of the three individual signals (Figures 7 & 8). On the corrected PSD spectra for each of the individual signals, the sets of spectral power amplitudes are within the following intervals: 0.1–1.0 Hz, 1.8–2.0 Hz and from 9.0 – 20 Hz (Figure 9). On the average spectrum referring to all the three signals (Figure 10), the dominant amplitudes of frequencies (in Hz) are: 0.22, 0.3, 0.45, 0.6 and 0.72 and there are small sets between 2.0-3.0 and 10-20 Hz. Small sets of noises with larger amplitudes (Figures 11 & 12) are singled out in the records of the three signals obtained on a weaker base (seismometer SS1_2251). On the PSD spectra (Figure 13) for the three corrected signals, there are important amplitudes of 0.12, 0.25, 0.40 and smaller amplitudes within two sets between 1.5 – 5.0 Hz and from 9 – 20 Hz. The shape of the average spectrum of the three measurements (Figure 14) is very similar to that of the three individual spectra, with occurrence of predominant frequencies on the same place. Figure 15 shows the comparison of the average spectra for both the seismometers. It is noted that, on the spectrum of the signals obtained on the weaker base (seismometer SS1_2251) there occurs large amplitude at 0.12 Hz that is due to the noise transferred through the weak base. The dominant frequencies occur at 0.2, 0.3 and 0.45 Hz, whereas the ratio of the spectral amplitudes is almost 5 times lower in the case of the tremor measured on a harder base (SS1_2238), in the frequency interval of 1-20 Hz.

**Figure 1.** PRZ (1): SS1_2238 (recordings of micro tremors on hard soil-rock seismometer location)

PRZ (2): SS1_2251 (recordings of micro tremors on medium soft soil seismometer location)
Figure 2. TSOFT presentation of seismic tremor recordings at PRZ location

Figure 3. PRZ (2); Spectrogram of micro tremors recording on medium soft soil location (seismometer SS1_2238)
Figure 4. PRZ (1): PSD spectrum of no corrected recording of micro tremors (SS1_2238)

Figure 5. PRZ (2): Spectrogram of micro tremors recording on medium soft soil location (seismometer SS1_2251)
Figure 6. PRZ (2): PSD spectrum of no corrected recording of micro tremors (SS1_2251)

Figure 7. PRZ (1): Segments (~40 s duration) of no corrected recording of micro tremors (SS1_2238)
Figure 8. TSOFT presentation of separated segments of seismic tremor recordings at PRZ (1) location

Figure 9. PRZ (1); PSD spectrum for 3 separated (8192 samples each) of corrected recording of micro tremors (SS1_2238)
Figure 10. PRZ (1): Averaged PSD spectrum for 3 separated PSD spectrums (8192 samples each) of corrected micro tremors recording (SS1_2238)

Figure 11. PRZ (2): Segments (~40 s duration) of no corrected recording of micro tremors (SS1_2251)
Figure 12. TSOFT presentation of separated segments of seismic tremor recordings at PRZ (2) location

Figure 13. PRZ (2): PSD spectrum for 3 separated (8192 samples each) of corrected recording of micro tremors (SS1_2251)
Figure 14. PRZ (2): Averaged PSD spectrum for 3 separated PSD spectrums (8192 samples each) of corrected micro tremors recording (SS1_2251)

Figure 15. PSD averaged spectrums (PSD_avr) for locations:

PRZ (1): PSD_cor_1; seismometer SS1_2238; PRZ (2): PSD_cor_2; seismometer SS1_2251

Conclusions:
Spectra were computed from the records and compared with the new low noise model. The performed micro tremor analysis enabled selection of the most favourable micro locations for seismological station of Prizren from the aspect of minimal seismic noise and providing of high quality earthquake records.
References: