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Exergy Analysis of the Process of Thermal Decomposition of Phosphogypsum to Lime and Sulfur Dioxide

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Abstract

The wet process phosphoric acid is produced by decomposition of phosphate raw materials with sulfuric acid. This gives a large amount of waste product - phosphogypsum. The thermochemical decomposition of phosphogypsum to lime and sulfur dioxide provides possibilities to utilize its main components CaO and S and, at the same time, to solve some ecological problems. The main problem arising with this method is that it needs a large consumption of primary energy carrier - natural gas. The aim of the present work is to study the process with the exergy method and find new effective methods and technological schemes to reduce energy consumption. It is suggested to decompose phosphogypsum using the products from the incomplete combustion of the natural gas with oxygen enriched air and using a preliminarily prepared reducing gas mixture.

Key words: exergy analysis, phosphogypsum

1. Introduction

The phosphate fertilizers are produced on the basis of wet process phosphoric acid prepared by decomposition of natural phosphates with sulfuric acid. The waste product is 4.5 to 6 t phosphogypsum per 1 t acid (100% P_2O_5). The annual production of phosphate fertilizers in Bulgaria gives about 1.5 mln t phosphogypsum, therefore, much effort is devoted to the development of methods for its utilization (Evenchik and Novikov 1990). Thermochemical decomposition of phosphogypsum to lime and sulfur dioxide provides possibilities to utilize its main components CaO and S and, at the same time, to solve some ecological problems (Gruncharov 1986, Gruncharov 1989). The main problem with this method is the large consumption of the primary energy carrier - natural gas. Possibilities for its decrease have constantly been sought since it is a basic task for the improvement of the process (Evenchik and Novikov 1990). For this purpose, one of the modern methods for thermodynamic analysis and assessment of the exergy efficiency of technological systems was used - the exergy method (Brodyansky et al. 1994, Szargut 1988).

The process of thermochemical decomposition of phosphogypsum in fluidized bed to phospholime and sulfur dioxide was carried out under industrial experimental conditions, followed by production of sulfuric acid. The basic technological parameters of the process were determined (Gruncharov 1986, Gruncharov 1989). Problems that remained to be solved were the utilization of the waste heat and development of an exergy efficient technological scheme for thermochemical decomposition of phosphogypsum.

Exergy analysis of a specific system for processing phosphogypsum to lime and sulfuric acid was made. It suggested the use of larger amount of sulfuric acid to dry the gas from the obtained acid. This, however, predetermined its low exergy efficiency. The structure of the system was not analyzed, nor the possibilities for its improvement to decrease exergy losses (Wheelock et al. 1968, Kostilkov et al. 1983).

The aim of the present work is to study the possibilities for decreasing energy consumption in the process of decomposition of phosphogypsum to lime and sulfur dioxide using the exergy method of thermodynamic analysis.

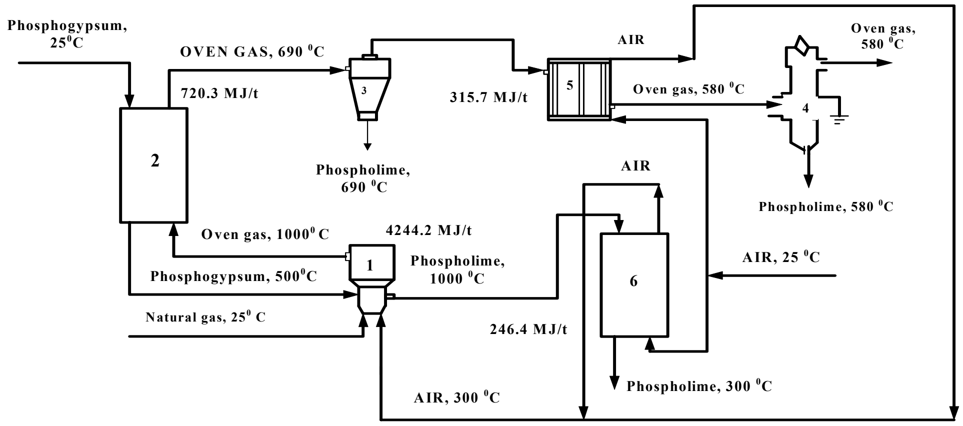

Figure 1. Oven aggregate for decomposing phosphogypsum into lime and SO_2, 1 - oven for phosphogypsum decomposition, 2,6 - direct heat exchangers, 3,4 - separators, 5 - indirect heat exchanger

2. Description of the Process of Thermochemical Decomposition of Phosphogypsum to Lime and Sulfur Dioxide using the products from the incomplete combustion of natural gas with air

The technological scheme is presented in *Figure 1*.

The phosphogypsum fed into the system contained (wt%): $CaSO_4.0,5H_2O$ - 80.00; $CaSO_4.2H_2O$ - 14.50; $Ca_5F(PO_4)_3$ - 0.97; $CaSiF_6$ - 2.30; $CaO.Al_2O_3.2SiO_2$ - 1.00; $CaHPO_4$ - 0.44; CaF_2 - 0.26; H_3PO_4 - 0.13; SiO_2 - 0.40.

Phosphogypsum directly contacts with oven gas in heat exchanger 2 where the following reactions occur: $CaSO_4.2H_2O$ is dehydrated at 107°C to $CaSO_4.0,5H_2O$ and $CaSO_4.0,5H_2O$ dehydrates at 200 - 210°C to $CaSO_4$. The released water goes into the gas phase. $CaSiF_6$ decomposes at 350°C (Pozin 1970), and from its products SiF_4 goes into the oven gas while CaF_2 remains as part of the phosphogypsum composition:

$$CaSiF_6=CaF_2+SiF_4 \qquad (1)$$

The main component of phosphogypsum fed into the oven was $CaSO_4$ (95 wt%) and the main component of the natural gas was CH_4 (92 vol.%). Heated air was also pumped into the oven. The main reaction of thermochemical decomposition of phosphogypsum is endothermal:

$$0,25CH_4 + CaSO_4 = CaO + SO_2 + 0,25CO_2 +$$
$$+ 0,5H_2O \quad \Delta H^0_{298} = +301.7 \text{ KJ.mol}^{-1} \ CaSO_4 \qquad (2)$$

To compensate for the endothermal reaction, natural gas is burned according to the reaction:

$$xCH_4 + 2xO_2 + yN_2 = xCO_2 + 2xH_2O +$$
$$+ yN_2 \quad \Delta H^0_{298} = -802.32 \text{ KJ.mol}^{-1} CH_4 \qquad (3)$$

The natural gas is used both as raw material according to reaction (2) and as fuel according to (3).

The following side reactions also take place in the oven:

$$CaF_2 + H_2O = CaO + 2HF \qquad (4)$$

$$CaO + 2H_3PO_4 = Ca(PO_3)_2 + 3H_2O \qquad (5)$$

$$2CaHPO_4 = Ca(PO_3)_2 + CaO + H_2O \qquad (6)$$

$$CaO.Al_2O_3.2SiO_2 + 6CaO = 3CaO.Al_2O_3 +$$
$$+ 2[2CaO.SiO_2] \qquad (7)$$

$$SiO_2 + 2CaO = 2CaO.SiO_2 \qquad (8)$$

The oven gas obtained containes (vol. %): SO_2 - 8.00; CO_2 - 10.24; H_2O - 20.64; N_2 - 60.71; HF - 0.41, while the phospholime obtained consists of (wt%): CaO - 83.78; $CaSO_4$- 4.28; $2CaO.SiO_2$ - 6.00; $3CaO.Al_2O_3$ - 2.41; $Ca_5F(PO_4)_3$ - 2.41; $Ca(PO_3)_2$ - 1.12.

3. Exergy Analysis of the Process of Thermochemical Decomposition of Phosphogypsum to Lime and Sulfur Dioxide Using the Products from the Incomplete Combustion of Natural Gas with Air

Exergy analysis of oven unit for production of lime and SO_2 by interaction between phosphogypsum and the products of incomplete combustion of natural gas with air was performed (*Figure 1*). The outgoing oven gas had a temperature of 580°C and the phospholime obtained was at 300°C. The natural gas consumption was 172 Nm^3/t phosphogypsum. The thermodynamical parameters studied were low (exergy efficiency 51.8%) due to the high internal and external exergy losses (TABLE I).

The losses observed by this technological process can be reduced by:

1. Reduction of the heat loss into the environment.

2. Increase of the degree of utilization of the heat from oven gas and phospholime obtained.

3. Optimization of the structure of the heat exchanging system.

A modified oven unit was designed to utilize to a higher extent the heat of the oven gas and phospholime for heating the natural gas and air, respectively. As a result, the outgoing oven gas temperature was reduced to 360°C and that of phospholime - to 100°C (*Figure 2*). The natural gas consumption was measured to be 154.8 Nm^3/t. The exergy efficiency, however, was 49.0% and the total exergy losses were 3097.4 MJ/t. The results obtained with the oven unit designed did no show other possibilities for heat utilization with the type and structure of the heat exchanging system used.

An optimal structure would allow improvement in heat utilization and reduction of investments in a new heat exchanging system.

Therefore, the heat exchanging system was optimized employing the method of Nishida (Nishida et al. 1971, 1981 and Hartmann 1982). As a result, the structure illustrated in *Figure 3* was constructed. It consisted of only three heat exchangers, one of them indirect and two direct. The natural gas consumption was further reduced to 151.4 Nm3/t.

The analysis of the results obtained showed, for the technology of thermochemical decomposition of phosphogypsum studied, no other possibilities for reduction of the energy consumption. Consequently, new methods for thermochemical decomposition of phosphogypsum were investigated, which would allow further reduction of the natural gas consumption used as fuel and/or raw material.

TABLE I. DISTRIBUTION OF THE EXERGY LOSSES

Source	External exergy loss		Internal exergy loss	
	MJ/t	%	MJ/t	%
Oven for phosphogypsum decomposition	844.9	91.86	1615.2	69.41
Heat exchanger for phosphogypsum	31.8	3.46	436.9	18.77
Heat exchanger for phospholime	30.4	3.31	69.8	3.00
Heat exchanger for oven gas	12.7	1.37	205.1	8.82
Total	919.8	100.00	2327.0	100.00

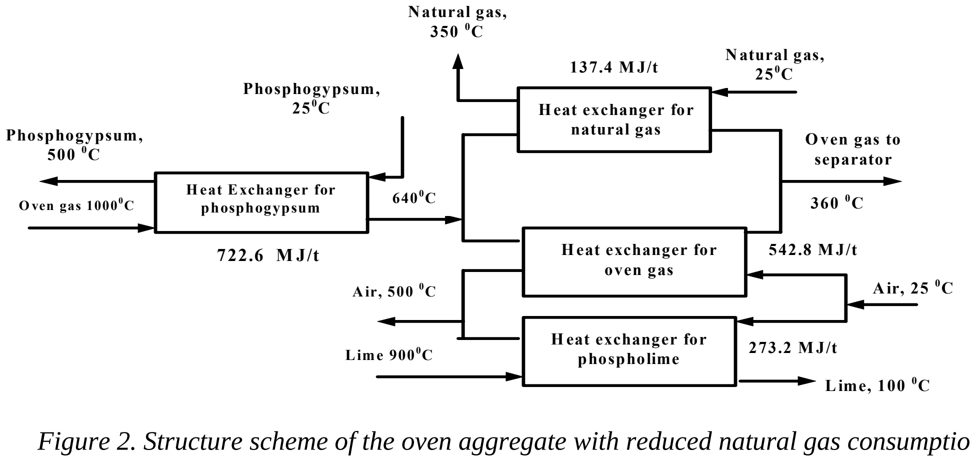

Figure 2. Structure scheme of the oven aggregate with reduced natural gas consumption

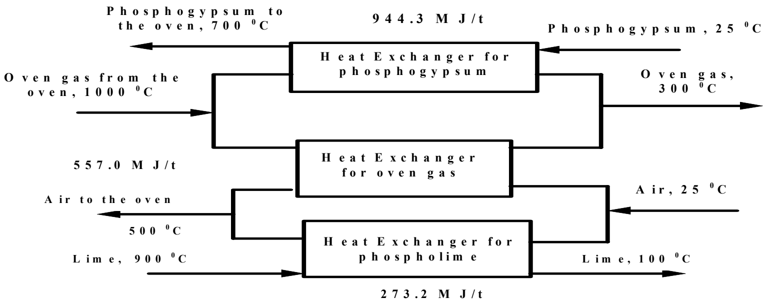

Figure 3. Structure scheme of heat exchanging system

4. Development of a Method for Thermochemical Decomposition of Phosphogypsum to Lime and Sulfur Dioxide Using the Products from the Incomplete Combustion of Natural Gas with Oxygen and Oxygen Enriched Air

The air fed into the oven contains a significant amount of nitrogen and the nitrogen content in the oven gas was measured to be ca 50%. Reduction or elimination of the nitrogen introduced into the system would improve the heat balance of the oven and the aggregate as a whole due to the reduction of the heat carried out of the aggregate with the oven gas at 300 °C. Besides, because of the small sizes of the oven and heat exchangers, the consumption of natural gas as fuel was expected to be significantly reduced if oxygen enriched air or technological oxygen (95% O_2) were fed into the system.

Optimal structure of the heat exchanging system was found for the oxygen concentrations from 25 to 95%. The structure illustrated in *Figure 4* is optimized for oxygen-enriched air containing 30% oxygen, while for low concentrations the structure depicted in *Figure 3* would be more effective. The exergy balances for these structures were calculated which allowed to determine their exergy efficiencies (TABLE II).

The use of oxygen enriched air was found to decrease the consumption of natural gas and both external and internal exergy losses, thus increasing the exergy efficiency of the system compared to the use of air (TABLE II). At O_2 concentration of 30% in the air, the natural gas consumption decreased from 151.4 Nm^3/t to 127.3 Nm^3/t and the exergy efficiency increased up to 59.20%. At 50% O_2 concentration the natural gas consumption was 118.7 Nm^3/t and the exergy efficiency - 61.76%. When technological oxygen (95% O2) was used, the exergy efficiency increased to 65% but the natural gas consumption remained unchanged (*Figure 5*).

Another positive effect observed with the use of oxygen enriched air that the increase of oxygen content to 50% gave 18% concentration of SO_2 in the oven gas and the volume of the oven gas was significantly lower (*Figure 6*).

As a result, the sizes of the oven and the heat exchangers can be reduced, which means that the cost of the oven aggregate and the cost of the processing of the oven gas to sulfuric acid would be much lower.

To estimate the actual exergy efficiency of the suggested method using oxygen enriched air, the energy consumption for production of oxygen should also be taken into account, as well as the consumption of primary energy carrier (natural gas) for production of the necessary electric power (Atanasova 1998).

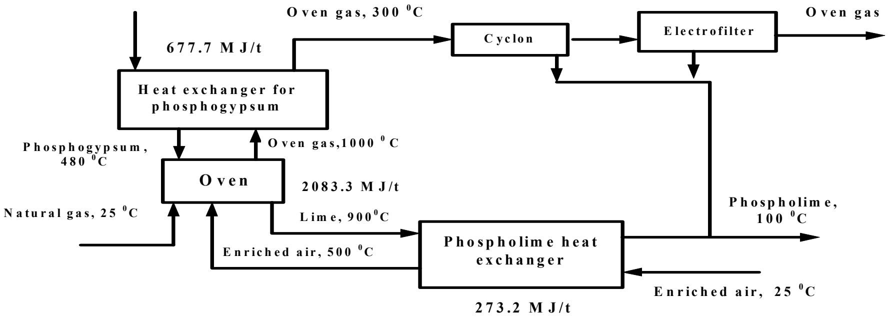

Figure 4. Structure scheme of the oven aggregate using oxygen enriched air

TABLE II. EXERGY EFFICIENCY OF THE OVEN AGGREGATE DEPENDING ON DIFFERENT OXYGEN CONCENTRATIONS IN ENRICHED AIR

Oxidation	Oxygen concentration , %	Useful exergy, MJ/t	Exergy consump-tion, MJ/t	Exergy losses, MJ/t			Exergy efficiency, %
				External	Internal	Total	
Air	21	3484.76	6731.59	919.51	2327.32	3246.83	51.77
Enriched air	30	2976.58	5029.63	541.79	1511.26	2053.05	59.20
	50	2907.72	4708.22	418.23	1382.27	1800.50	61.76
	95	3071.14	4725.31	357.49	1296.68	1654.17	65.00

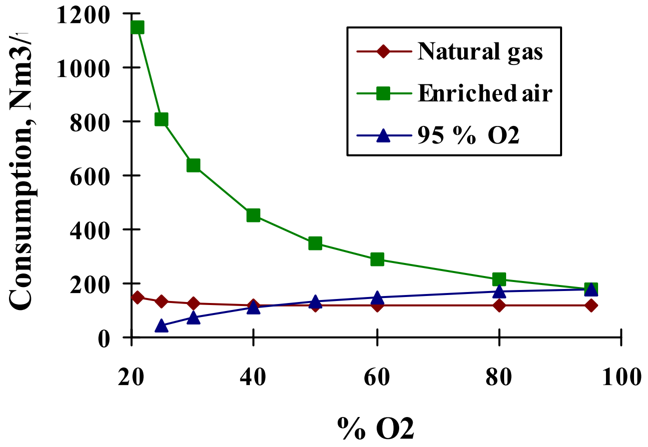

Figure 5. Effect of the oxygen concentration in the enriched air on the consumption of natural gas, enriched air and 95% O_2 used for the air enrichment

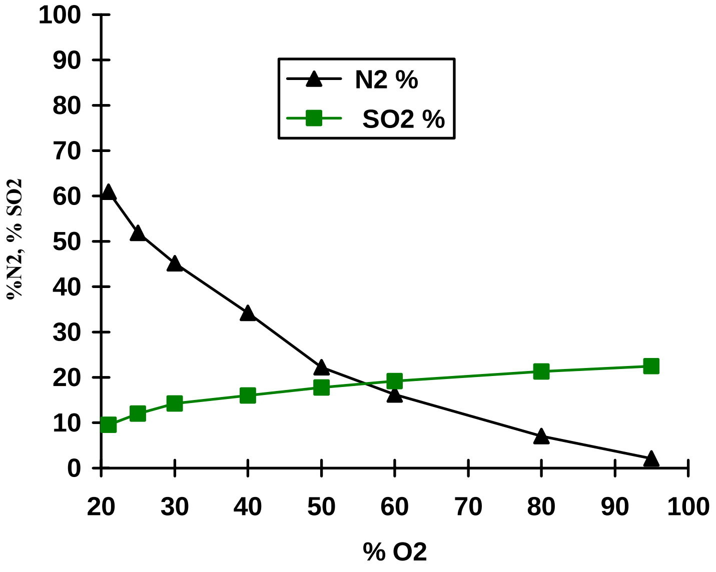

Figure 6. Effect of the oxygen concentration in the enriched air on the nitrogen and SO_2 content in the oven gas

The dependence of the total exergy consumption and exergy efficiency of the system “Oven aggregate - Production of oxygen - Thermal power station” on the oxygen concentration in the enriched air, on electric power consumption for production of oxygen (within 0.3 to 0.8 kWh/Nm^3 O_2) and on exergy efficiency of the thermal power station (from 0.36 to 0.46) were studied (Springman 1977). The optimal concentration of oxygen in the enriched air was found to be 50% in the range 0.3 - 0.6 kWh/Nm^3, regardless of the exergy efficiency of the power station (Atanasova 1998). At high values of the power station efficiency (0.46) and low consumption of electric power for production of technology oxygen (0.3 kWh/Nm^3 O_2), the optimal concentration of oxygen in the enriched air can be higher than 50% (Atanasova 1998).

The results obtained showed that the exergy efficiency of the thermochemical decomposition of phosphogypsum using oxygen-enriched air depends on the effectiveness of the methods for production of technological oxygen and electric power.

5. Development of a Method for Thermochemical Decomposition of Phospho- Gypsum to Lime and SO_2 with Separate Production and Usage of Reducing Gas

The thermodynamic analysis of the decomposition of phosphogypsum to lime and sulfur dioxide showed that about 30.5% of the total consumption of natural gas was used to compensate for the heat from the endothermal interaction of the phosphogypsum according to reaction (2) (Kirova et al. 1985). A possible way to decrease the natural gas consumption is to separate reaction (2) into 2 stages and carry out the first of them out of the oven:

I stage:

$$CH_4 + H_2O = CO + 3H_2 \qquad \Delta H^0_{298} = +206.3 \text{ KJ.mol}^{-1}\ CH_4 \qquad (9)$$

II stage:

$$CaSO_4 + H_2 = CaO + SO_2 + H_2O \qquad \Delta H^0_{298} = +260.3 \text{ KJ.mol}^{-1}\ CaSO_4 \qquad (10)$$

$$CaSO_4 + CO = CaO + SO_2 + CO_2 \qquad \Delta H^0_{298} = +219.2 \text{ KJ.mol}^{-1}\ CaSO_4 \qquad (11)$$

The first stage, preparation of reducing gaseous mixture of H_2 and CO by catalytic steam conversion of natural gas in a tube furnace, is a widely used industrial process. The reducing gaseous mixture obtained contained (vol. %): CO_2-0.57; H_2-71.27; CO-23.62; CH_4-0.87; N_2-0.77; H_2O-2.90. The heat necessary to carry out the endothermal reaction (9) is usually supplied by burning fuel and is introduced in the reaction mixture through indirect heat exchange (Nielsen - Rostrup J. R 1975).

The second stage, the interaction between $CaSO_4$ with H_2 and CO, is carried out in the oven aggregate. The combustion of natural gas to make the process self-heating takes place in the oven for decomposition of phosphogypsum. The positive effect from the separation of the reaction into two stages results from the decrease of the inert component (nitrogen) carried with the air used for the combustion.

The calculation of the exergy efficiency of the oven aggregate using reducing gaseous mixture should involve determination of the total energy consumption of the combined system consisting of two parts: the oven for decomposition of phosphogypsum and the tube furnace for preparation of reducing gas. Thus, the total consumption of natural gas for both subsystems would be taken into account (*Figure 7*).

For this purpose, exergy analysis of the thermochemical decomposition of phosphogypsum to lime and sulfur dioxide using reducing gaseous mixture (prepared separately by steam conversion of natural gas) was made. Two modifications were studied. In the first one, the combustion of natural gas in the oven for decomposition of phosphogypsum was maintained with plain air while the second one involved oxygen-enriched air (30% O_2) (TABLES III, IV). The natural gas consumption was reduced (126.5 Nm^3/t by the first modification and 120.5 Nm^3/t by the second one), the exergy efficiencies of the oven aggregate for both modifications increased to 66-67% (TABLE V) and the total exergy efficiency of the combined system (oven aggregate and reducing gas preparation) for both modifications was 59.0 and 59.6%, respectively.

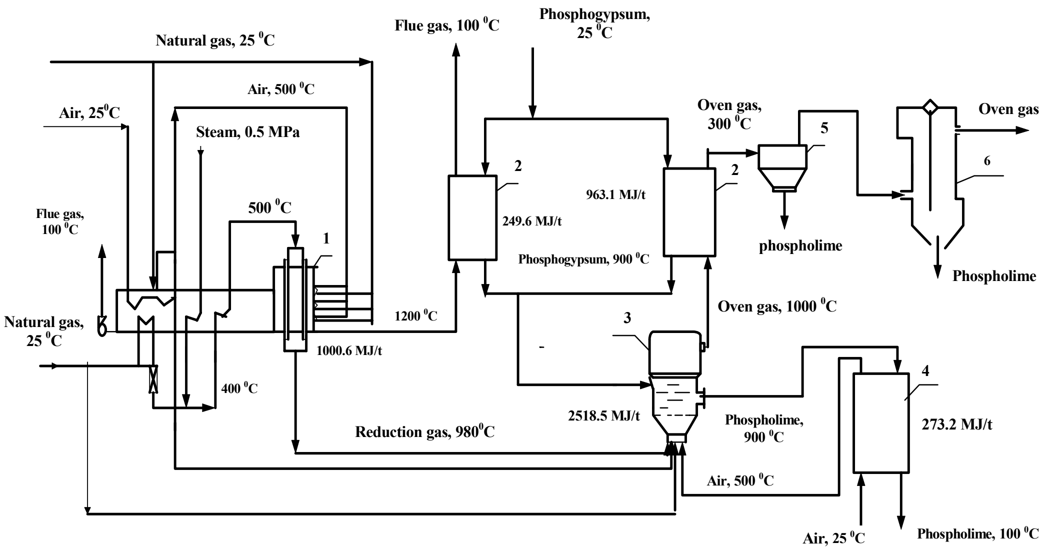

Figure 7. Energy integrated system for thermochemical decomposition of phosphogypsum to lime and SO_2 with preliminarily prepared reducinggas

1 - tube furnace, 2.4 - direct heat exchangers, 3 - oven for the phosphogypsum decomposition, 5,6-separators

TABLE III. EXERGY BALANCE OF THE SYSTEM "OVEN AGGREGATE AND PRELIMINARILY PREPARED REDUCING GAS PRODUCTION", USING AIR

Flow	**Input exergy, MJ/t**	**Flow**	**Output exergy, MJ/t**
Phosphogypsum	185.42	Phospholime	795.39
Technological natural gas to the tube furnace	1304.88	SO_2 – containing gas	2172.71
Fuel natural gas to the tube furnace	1034.78	Useful exergy	2968.10
Natural gas to oven aggregate	2472.82	External losses with:	778.68
Combustion air	-	– flue gas	36.18
Air to the oven for decomposition of phosphogypsum	-	– heat losses	742.50
Steam	28.07	Internal losses	1279.19
		Total losses	2057.87
Total	5025.97	Total	5025.97
η_e = = **0 . 5905**			

TABLE IV. EXERGY BALANCE OF THE SYSTEM "OVEN AGGREGATE AND PRELIMINARILY PREPARED REDUCING GAS PRODUCTION", USING OXYGEN ENRICHED AIR (30% O_2)

Flow	**Input exergy, MJ/t**	**Flow**	**Output exergy, MJ/t**
Phosphogypsum	185.42	Phospholime	795.39
Technological natural gas to the tube furnace	1304.88	SO_2 – containing gas	2065.93
Fuel natural gas to the tube furnace	1186.95	Useful exergy	2861.32
Natural gas to oven aggregate	2092.38	External losses with:	687.75
Combustion air	–	– flue gas	40.76
Oxygen enriched air (30% O_2) to the oven for decomposition of phosphogypsum	2.27	– heat losses	646.99
Steam	28.07	Internal losses	1250.90

		Total losses	1938.65
Total	4799.97	Total	4798.97
η_e =0.5961			

TABLE V. COMPARISON OF THE EXERGY EFFICIENCIES OF THE DIFFERENT METHODS FOR THERMOCHEMICAL DECOMPOSITION OF PHOSPHOGYPSUM

Process	**Natural gas consumption, Nm^3/t**		**Exergy efficiency, %**	
	Oven aggregate	**Whole system**	**Oven aggregate**	**Whole system**
Thermochemical decomposition of phosphogypsum by reduction with the products of the partial oxidation of natural gas with air	154.8	154.8	49.0	49.0
Thermochemical decomposition of phosphogypsum by reduction with the products of the partial oxidation of natural gas with:				
– oxygen-enriched air (30%)	127.3	137.0	59.2	55.6
– technological oxygen (95%)	118.7	141.2	65.0	55.3
Thermochemical decomposition of phosphogypsum with preliminarily prepared reducer gas and with:				
- air for the oven aggregate	65.0	126.5	65.6	59.0
- oxygen-enriched air (30%) for the oven aggregate	55.0	126.2	66.8	57.1

The actual energy consumption for production of technological oxygen necessary for the enrichment of the air for the second modification was also taken into account. The use of both oxygen enriched air and separate production of reducing gaseous mixture was found to be ineffective (TABLE V).

The efficiency of the combined process was higher than that of the process using oxygen enriched air (TABLE V). It can be explained with the higher effectiveness of the process for production of reducing gaseous mixture compared to the processes production of oxygen and electric power (TABLE V).

The results obtained from the analysis of the different methods and energy integrated systems lead to the conclusion that, with optimized structure of the oven aggregate, the efficiency of the method depends heavily on the efficiencies of the accompanying systems (production of oxygen, electric power and reduction of the gaseous mixture).

6. Conclusion

Using the exergy method for analysis, some energy integrated problems connected with the thermochemical decomposition of waste phosphogypsum to lime and sulfur dioxide were studied. From the results obtained, the following conclusions can be made:

1. Exergy analysis of the process of thermochemical decomposition of phosphogypsum to lime and sulfur dioxide with the products of the partial oxidation of natural gas with air was carried out. The oven aggregate was found to have low exergy efficiency (51.8%). It was shown that natural gas consumption can be reduced by improving the utilization of the heats of the oven gas and phospholime obtained and by reducing the heat loss. The structure of the oven aggregate was improved and the basic parameters of the process were increased to achieve reduction of natural gas consumption by ca. 10%.

2. Based on the exergy analysis, two new methods for thermochemical decomposition of phosphogypsum to lime and SO_2 were developed: using the products of the partial oxidation of natural gas with oxygen enriched air, and using a preliminarily prepared reducing gaseous mixture. The exergy efficiency of the oven aggregate was observed to increase, as well as the SO_2 concentration in the oven gas. The size of the equipment and, correspondingly, the gas treatment costs were also reduced. The process involving reducing gaseous mixture was found to be the better alternative because the production of reducing gas is more effective compared to the production of both oxygen and electric power.

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