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AMAÇ VE KAPSAM

Bilimsel Madencilik Dergisi TMMOB Maden Mühendisleri Odası'nın açık erişimli elektronik ortamda ve basılı olarak yayımlanan süreli bilimsel yayınıdır. Dergi 1960 yılından itibaren yayımlanmaktadır. Derginin ismi 2016 yılı Haziran sayısına kadar "Madencilik" şeklindeyken, benzer isimli popüler dergilerle karıştırılabilmesi nedeniyle 2016 yılı Eylül sayısından itibaren "Bilimsel Madencilik Dergisi" olarak değiştirilmiş ve o tarihe kadar 0024-9416 olan ISSN numarası da 2564-7024 olarak güncellenmiştir.

Yılda 4 kez (Mart-Haziran-Eylül-Aralık) yayımlanan Bilimsel Madencilik Dergisi (ISSN: 2564-7024), maden mühendisliği ve mineral endüstrisi alanında ulusal ve uluslararası düzeyde yapılan, bilimsel normlara ve yayın etiğine uygun, özgün bilimsel çalışmaları bilim insanlarına, maden mühendislerine ve kamuoyuna duyurmayı ve bu yolla bilimsel bilgiyi toplumla paylaşmayı amaçlamaktadır. Derginin yayın dili Türkçe ve İngilizce'dir.

Dergi, maden mühendisliği alanında özgün bir araştırmayı bulgu ve sonuçları ile yansıtan kuramsal, deneysel ve uygulamalı araştırma makalelerine; yeterli sayıda bilimsel makaleyi tarayıp konuyu bugünkü bilgi ve teknoloji düzeyinde özetleyen, değerlendirme yapan ve bu bulguları karşılaştırarak yorumlayan tarama makalelerine; özgün bir yöntem veya tekniği tarif eden kısa makale olarak tanımlanabilecek teknik notlara; ve gerçek ya da kuramsal bir mesleki uygulamayı temel alan, sistematik veri toplama ve veri analizi içeren vaka çalışmalarına yer vermektedir.

Dergide, yenilenemeyen maden kaynakların sürdürülebilir madencilik ilkeleri doğrultusunda insanlığın hizmetine sunulması için gereken mevcut bilginin geliştirilmesini sağlayacak konularda eserlere öncelik verilmektedir. Bu kapsamda; maden arama, maden yatağı modelleme, topoğrafya, maden ekonomisi, jeoistatistik, kaya mekaniği ve jeoteknik, kazılabilirlik etüdü, yer altı ve açık maden işletme, maden tasarımı, madenlerde ve tünellerde tahkimat sistemleri, delme-patlatma tasarımı, madenlerde üretim planlaması ve optimizasyon, madenlerde iş sağlığı ve güvenliği yönetimi, maden havalandırma, yeraltı kömür madenlerinde metan gazı emisyonu ve metan drenajı, cevher hazırlama ve zenginleştirme, proses mineralojisi, analitik teknikler, öğütme, sınıflandırma ve ayırma, flotasyon/flokülasyon, katı/sıvı ayırımı, fiziksel zenginleştirme yöntemleri, hidro ve biyometalurji, üretim metalurjisi, modelleme ve simülasyon, enstrümantasyon ve proses kontrol, geri dönüşüm ve atıkların işlenmesi, maden hukuku, madenlerde çevre sağlığı ve yönetimi, madenlerde nakliyat, makina ve ekipman seçimi ve planlaması, kömür gazlaştırma, mermer teknolojisi, endüstriyel hammaddeler, uzay madenciliği, denizaltı madenciliği ve mekanizasyon ile ilgili konular dergi içeriğinde yer almaktadır.

Gönderilen yazılar editörler kurulu ve konusunda uzman hakemler tarafından bağımsız ve akademik yayıncılıkta en iyi uygulamalarla uyumlu şekilde değerlendirilmekte olup, değerlendirme süreci sonunda yayınlanması uygun görülen yazıların yayın hakları yazarlar tarafından telif sözleşmesi ile TMMOB Maden Mühendisleri Odası'na devredilir.

AIMS AND SCOPE

Scientific Mining Journal, which is published in open access electronic environment and in printed, is a periodical scientific journal of Union of Chambers of Turkish Engineers and Architects Chamber of Mining Engineers. The name of the journal was "Mining" until June 2016 and it has been changed to "Scientific Mining Journal" since September 2016 because it can be confused with popular journals with similar names and the ISSN number has been updated from 0024-9416 to 2564-7024.

Scientific Mining Journal, published four times a year (March-June-September-December), aims to disseminate original scientific studies which are conducted according to the scientific norms and publication ethics at national and international scale, to scientists, mining engineers, the public; and thus to share scientific knowledge with society. The journal is in both Turkish and English.

The journal covers theoretical, experimental, and applied research articles, which reflects the findings and results of an original research in the field of mining engineering; review articles, which assess, evaluates, and interprets the findings of a comprehensive review of sufficient number of scientific articles and summarize them at present information and technology level; technical notes, which may be defined as a short article that describes a novel methodology or technique; a case studies, which are based on the theoretical or real professional practice and involves systematic data collection and analysis.

The journal gives priority to works that will enable the advancement of current available information necessary to serve humanity with nonrenewable mineral resources with the perspective of sustainable mining principles. In this context, mine exploration, mineral resource modeling, surveying, mine economics and feasibility, geostatistics, rock mechanics and geotechnics, diggability studies, underground and surface mining, mine design, support design in underground mines and tunnels, rock penetration and rock fragmentation, mine production planning and pit optimization, mine health and safety management, mine ventilation, methane emission and drainage in underground coal mines, mineral processing and beneficiation, process mineralogy, analytical techniques, mineral comminution, mineral classification and separation, flotation/flocculation, solid/liquid separation, physical enrichment methods, hydro and biometallurgy, production metallurgy, modeling and simulation, instrumentation and process control, recycling and waste processing, mining law, environmental health and management, transportation, machinery and equipment selection and planning, coal gasification, marble technology, industrial minerals, space mining, submarine mining and mechanization are included in the journal content.

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Original Research

An investigation into the enrichment of coal wastes of Western Lignite Company (WLC) by physical and physico-chemical methods

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A B S T R A C T

Mechanical excavation and the successive processes of coal production are the main reason for the occurrence of fine waste coals. These wastes are normally discharged without being processed from coal washing plants (-1 mm) which cause not only economic loses but also severe environmental problems. Therefore, it was attempted to enrich waste coals of WLC by using physical and physico-chemical methods and the results were compared.

From the tests, the optimum carbon content and the combustible recovery values were obtained as 85% and 97%, respectively, when sink-float method and the coarse particle size group were chosen. From the tests with the medium particle size group using spiral and Knelson separators, a combustible recovery of up to 90% was reached together with a carbon content of 80%. Moreover, a carbon content of 86.5% with a combustible recovery of 56.6% was obtained by using MGS. In the fine particle size group, the highest combustible recovery was obtained by using spiral and Knelson separators. The highest carbon content in the fine particle size group was reached through MGS and Jameson Cell.

Keywords: *Coal slimes, Flotation, Physical processing methods, Waste coal.*

Introduction

Coal is still the main fossil fuel that supplies 40% of total world energy demand (Xia et al., 2015; Meshram et al., 2015; Sivrikaya, 2014). On the other hand, coal comes out as the main energy resources in countries with limited energy resources because of high petroleum and natural gas prices. Therefore, maximum utilization of coal reserves in such countries is of utmost importance. Increased rate of mechanization and the successive processes used in coal production cause occurrence of a large amount of fine waste coals and decreases in plant performances. Hence, large amounts of coal waste are discharged to nearby waste ponds. This situation inevitably causes not only economic loses but also severe environmental problems (Chaurasia and Nikkam, 2016). Environmental effects caused by coal-related pollutants such as the acidic nature of pyrite within coal and new regulations about discharging coal wastes have recently caused mining companies and the researchers to focus on the possible enrichment of such wastes (Bahri and Karamoozian, 2012). Proper deposition or recycling of these fine coal wastes using effective methods or technologies are therefore, of highest importance for the mining industry in order to remove the environmental barriers for their growth and survival. For this purpose, alternative approaches such as partial or total enrichment of coals from the wastes or isolating the wastes after the dewatering process in suitable deposits to prevent environmental problems should be considered. This will enable the recycling of such coal wastes instead of discharging to the environment, which in turn, provide economic gains and environmental protection (GEM, 2019).

The universal problem with regard to fine waste coals also exists in Turkey. For example, fine coal bearing wastes of 2.5 million m^3 have been discharged yearly from the coal mine of the WLC for which the current research was carried out. Unfortunately, these wastes are not being used in the coal powered station nearby, mainly because of the high dewatering cost required. The other problem being faced with regard to the wastes of WLC is the cost of deposition is getting rather high for the company owing to strict legislation concerning the deposition of such wastes (Turkey, 2015). It is well known that most of the waste ponds are

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almost full with a total amount of wastes reaching up to 18 million m^3. Moreover, the newly created deposition areas such as the old open cast areas are being filled up rapidly. Therefore, the task of processing these fine waste coals is essential not only for economic reasons but also to comply with the legislation for the protection of environment.

From the literature reviewed, it was found out that some physical and physico-chemical methods were seen to be effective for the processing of fine coal wastes. As a matter of fact, various processing equipment ranging from jigs to heavy media separators and from cyclones to spiral separators have been successfully used in many coal processing plants in the world. New equipment such as Multi gravity separator (MGS), Knelson concentrator (KC), Falcon separator, spirals and heavy media cyclones based on the centrifugal forces have recently been employed for the separation and enrichment of fine waste coals.

Research attention has recently been drawn to spirals in removing the ash producing impurities within coal owing to the advantages they have, such as being economical, simple and solid in structure (no movable parts) (Honaker et al., 2006; Honaker, et al., 2013; Oney, 2013). While higher combustible recovery values have been obtained from the tests carried out using coal samples with low ash content, combustible recovery values typically decrease as ash content increases. Research interest has also increased on the use of KC for the processing of fine coals where spirals possess some difficulties. Honaker et al. (1996), obtained a clean coal of 8% ash content with a high combustible recovery from the tests on medium sized coals with low ash content. A clean coal with 16.28% ash content was obtained with a combustible recovery of 67.82% from a hard coal having an ash content of 34.30% by Öney and Tanrıverdi (2016). Uslu et al. (2012), reported that they had removed ash content with a high combustible recovery at a particle size group of -0.500+0.300 mm. A clean coal having 30.51% ash was obtained by Sabah and Koltka (2014) from the samples with high ash content taken from a waste pond.

Processing attempts using spirals on fine particle sizes have been very limited. Honaker et al. (2007) reached a clean coal of 11.71% ash content through a combustible recovery of 84% after processing by spirals on coals with a 33.5% ash content. Moreover, a clean coal of 8% ash content was obtained by 70% combustible recovery by Honaker and Das (2004) using KC on fine coals with a 22% ash content.

Although the MGS application is more common for the processing of chromium ores, there has also been a growing tendency for the use of MGS in coal enrichment. Many investigations have been carried out by using MGS on both run-of-mine coal with high ash content (Aslan et al., 1999; Oz Aksoy et al., 2012a; Oz Aksoy, et al., 2012b; Oz Aksoy et al., 2014) and on the medium and fine particle sized waste coals taken from waste ponds or coal processing plants (Altun et al., 2010; Cicek et al., 2008; Engin et al., 2006; Erdem et al., 2008; Erdem et al., 2012).

Physico-chemical methods have found increasing uses for the processing of finer coal wastes together with physical methods. Coal is typically known as an organic and naturally hydrophobic substance having some inorganic impurities. However, floatability of coal particles is a complex process determined by various factors owing to the complex chemical nature of coal. Although, presence of functional chemical groups within coal such as (carboxyl (-COOH), carbonyl (-C=O), and hydroxyl (phenolic –OH)) are thought to be the main reason for the floatability of coal surfaces, the other factors such as surface elemental composition, surface morphology and particle size also play important roles in the hydrophobicity of coal surfaces (Bunt, 1997; Piñeres et al., 2018; Polat et al., 2003; Sivrikaya, 2014; Sokolović et al., 2012; Tao et al., 2002; Wang and Tao, 2018; Xia etal., 2017). Since the hydrophobicity of coal samples taken from waste ponds is decreased because of the oxidation process, it is required to use an excessive amount of fuel oil (Tao et al., 2002). Therefore, ash content of most Turkish coals could not adequately be reduced by using the flotation method only (Sivrikaya, 2014; Oz Aksoy et al., 2010; Oz Aksoy et al., 2014). As a matter of fact, meaningful results were not obtained from many enrichment tests on highly oxidised coal wastes using mechanical flotation (Engin et al., 2008) and column flotation (Oteyaka et al., 2008). However, a clean coal of 18.3% ash content was obtained with a high combustible recovery by using the Jameson Cell (Ucar et al., 2006). Das et al. (2010), were able to reduce ash content by 50% by using the Jameson Cell in the processing of coking coals with an ash content of 26%; the combustible recovery was 54%.

In this research, enrichment possibilities of fine waste coals were investigated using various physical and physico-chemical methods which are commonly used for ore processing and the comparisons of the aforementioned methods were made. This research can, therefore, be stated as the first comprehensive study which compares the results of various enrichment methods for the wastes of a coal processing plant in Kütahya-Turkey. For this purpose, various methods such as sink-float, spiral separator, KC, MGS and different types of flotation cells were used. The waste pond material was also investigated in terms of their particle size distribution, mineralogy and fractional chemical composition. Effective enrichment performance for the processing of wastes ranging from coarse to fine was determined both by using the equipment working on centrifugal forces and flotation principles; more specifically by using classical and Jameson Cells. Finally, comparisons were made according to the particle size fractions and the equipment used.

1. Materials and methods

1.1. Materials

The samples used during the tests were collected from the waste pond of WLC called Number-4. The pond covers an area of 163637 m^2 with a waste capacity of 3960000 tons. Samples were collected by WLC personnel using an excavator, however, sampling points were determined by the researchers. Samples were collected by 50 m intervals and from the deepest part of the pond that the excavator arm could reach. Two buckets of samples (approximately 2 tons) were excavated from each excavation point. The samples obtained were first mixed-homogenized and later the amount of samples were reduced, near the pond, for delivery to the Mining Laboratory of Dumlupınar University. Approximately 400 kg of the material was taken to the laboratory and then they were re-mixed and homogenised. Homogenized materials were stored after being divided by the coning-and-quartering procedure for use in the following experiments. A Russel-Sieve was used for the proper classification of the material such as in 1, 0.212 and 0.038 mm particle sizes. -0.038 mm sized material was separated by sieving.

1.2. Characterisation

Particle size, chemical (elements, humidity, ash, sulphur and calorific value) and mineralogical analyses were made for the characterisation of the material used. Sieve analysis of the waste material taken from the pond was made in order to determine the cumulative amount of material for any particle fraction chosen and the results are summarised in Figure 1. As seen from Figure 1, waste material taken from the pond exhibits homogeneous distribution at fine particle fractions. Although, the largest particle size is 4 mm, 80% of the samples are finer than 0.150 mm. Under-sieve rate of 0.038 mm is seen to be 69.55%.

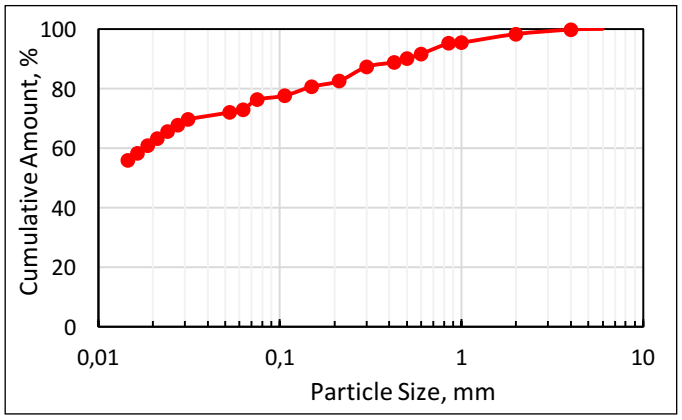

Figure 1. *Particle size distribution of the sample*

Elemental analysis of the material was made using an XRF instrument-of Panalytical brand (Axios Max model). Results of the elemental analysis for the samples taken from the waste pond are given in Table 1.

When Table 1 is examined, it is seen that major oxides are comprised of SiO_2, Al_2O_3, Fe_2O_3, CaO, MgO, K_2O and SO_3. Total amount of Na_2O and TiO_2 compounds within the sample is less than 1%. The reason for the high concentration of SiO_2, Al_2O_3 and Fe_2O_3 are explained by the existence of silica and clay minerals as gang (waste) or neighbouring minerals within the coal.

Coal wastes were classified into various particle size groups through sieving. The results for moisture, ash and sulphur contents, lower calorific value (LCV) and upper calorific value (UCV) of these particle size groups are given in Table 2.

As seen from Table 2, calorific values typically decrease while ash content increases as the particle size decreases. This result can be explained by the fact that clay minerals have fine particles and, therefore, they mostly pass into finer particle size groups. This result is even more noticeable in the materials under 38 microns.

Mineralogical analysis of the samples was made using an XRD instrument called PANalytical-Empyrean series using CuKαX-rays (λ=1.54 Å) in the range of 2θ=5–70° and at a rate of 2°/min. When XRD patterns of the samples are examined (Figure 2), it is seen that the dominant minerals are composed of quartz, muscovite/illite, montmorillonite, kristobalite, kaolinite, gypsum and pyrite.

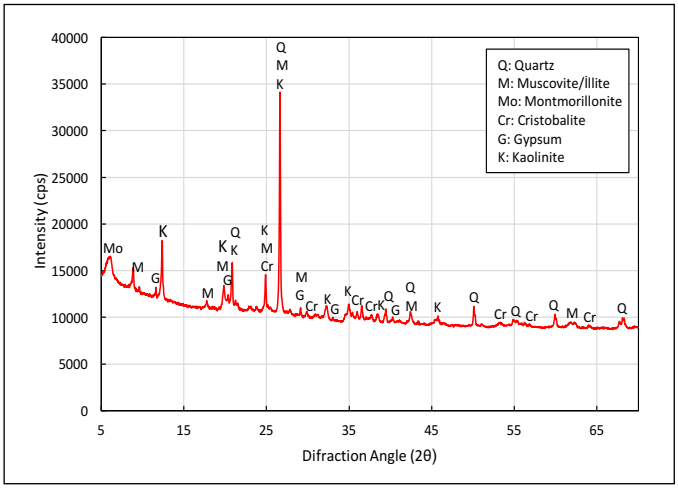

Figure 2. *XRD pattern of the sample*

Table 1. *Results of elemental analysis of the sample*

Compound	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	TiO_2	SO_3	LOI
Amount (%)	37.40	14.06	7.07	1.05	2.42	1.73	0.16	0.70	2.01	33.3

Table 2. *The results of humidity, ash content, LCV and UCV of the sample*

Particle Size (mm)	Weight (%)	Ash (%)	UCV (kcal/kg)	LCV, (kcal/kg)	Sulphur, (%)	Moisture, (%)
+4	0.24	27.25	5191	4763	1.07	3.80
-4+2	1.50	24.83	5441	4944	1.16	4.70
-2+1	2.87	20.41	5731	5233	1.19	4.30
-1+0.85	0.24	25.45	5170	4710	1.23	4.30
-0.85+0.6	3.55	22.31	5468	4980	1.24	4.40
-0.6+0.5	1.61	26.00	5260	4803	1.28	4.20
-0.5+0.425	1.23	26.66	5031	4564	1.26	4.60
-0.425+0.3	1.52	33.64	4859	4451	1.20	4.00
-0.3+0.212	4.78	40.04	4519	4133	1.33	4.20
-0.212+0.150	1.86	40.78	4670	4251	1.33	4.60
-0.150+0.106	3.06	47.1	3933	3680	1.43	2.20
-0.106+0.075	1.35	48.03	3358	3086	1.39	3.10
-0.075+0.063	3.33	49.07	3598	3263	1.31	3.90
-0.063+0.053	0.93	50.69	3127	2870	1.12	3.10
-0.053+0.038	2.37	58.81	2531	2333	1.11	2.50
-0.038	69.55	81.91	-	-	0.34	1.70
Total	100.00	68.01	-	-	0.62	2.35

1.3. Methods

The enrichment possibility of the samples taken from the waste pond called Number-4 was investigated in terms of their particle size distribution. Enrichment process was carried out in two stages, namely, the -0.038 mm sized materials with almost no coal content were first removed and the remaining materials were then processed. Samples were classified as coarse (+1 mm), medium (-1+0.212 mm) and fine (-0.212+0.038 mm) and the tests were carried out using these fraction groups of the samples. However, the ultra-fine fraction of the samples (-0.038 mm) being the largest portion (69.55%) but with high ash content (81.91%) and low calorific value was not used during the investigation. Two different enrichment methods, namely physical and physico-chemical methods, were employed throughout the research. Gravity based methods such as sink-float, spiral, KC and MGS were used for the physical processing. On the other hand, flotation method was employed with the mechanical and Jameson type of flotation cells for the physico-chemical processing of fine fraction group only. Sink-float processing method was preferred for the coarse fraction of the samples; the other gravity methods were used for both fine and medium size groups.

The most important performance assessment methods for processing are upgrading curves such as Halbich and Fuerstenau Curves (Duchnowska and Drzymala, 2012). In this research, Halbich Curves were used for the performance assessments or for the comparison of various processing methods employed.

1.3.1. Physical enrichment

In this research, the coarse fraction of the samples was processed by using sink-float method while the gravity based equipment such as Spiral, KC and MGS were used for the processing of other size groups.

1.3.1.1. Sink-float tests

In ASTM method D4371-06, sink-float processing method is fully described. Standard float-sink processes include adding predetermined amounts of representative coal samples into liquids with known densities or a range of densities, after classifying the samples to a specific particle size. Compared to clay, coal has relatively lower specific gravity (1.2 to 1.5). As a result, float-sink tests are typically conducted in liquids with densities ranging from 1.3 to 2.0. These densities were prepared by using $ZnCl_2$. Because coal has a lower density than the mass of clay, it floats in liquids with densities that are equivalent to or higher than coal, while clay sink.

The floating material is evaluated by scraping it off the top of the test tank, drying it, and weighing it to determine the float fraction based on the density of the liquid. The float fraction's ash content is also measured. Then, the graphs are drawn. In such an evaluation, various methods such as Henry Rheinhard Curves, Mayer Curve, Washability Index and MCM Curve are typically utilized (Arslan and Kemal, 2006; Meyers, 2012; Subba Rao and Gourichaaran, 2016; Unlu, 1990). More specifically, these methods indicate maximum coal quality to be reached after coal washing processes. Henry Rheinhard Curves were used to evaluate coal washing performance after the float-sink tests during this investigation.

1.3.1.2. Spiral

A laboratory type of Spiral having 5 curvatures and a diameter of 12.5 cm was used. The effects of feeding rate and solid rate to carbon content and combustible recovery values were determined for the fine and medium size fractions during the tests. Samples were collected by intervals both from the concentrate and the waste during testing without changing the descent angle of the equipment. The Spiral was used for the processing of the fine and medium size fractions. The spiral experimental conditions were (Table 3):

Table 3. *Spiral experimental operating conditions*

Parameters	Values
Descent angle (°)	90
Feeding rate (l/min)	5, 10, 15
Solid ratio (%)	10, 20, 30

The optimum results from the tests with medium size fraction were obtained as 30% and 10 l/min for the solid ratio and feeding rate, respectively. However, the optimum results from the tests with the fine fraction were obtained as 20% and 15 l/min for the solid ratio and feeding rate, respectively.

1.3.1.3. Knelson concentrator (KC)

Fine and medium size fractions of the samples were processed by using a laboratory type of KC (KC-MD3). Test were accomplished by changing water flow rates and the rotational speed of conical bowl on both fractions. The KC experimental conditions were (Table 4):

Table 4. *KC experimental operating conditions*

Parameters	Values
Solid ratio (%)	10
Rotational speed (rpm)	20, 30, 40, 50
Water flow rate (l/min)	2, 3, 4

Samples were fed to the KC at a solid ratio of 10% and the overflow (clean coal) was collected in a concentrate bowl while the underflow (waste) was retained by the KC chamber. Clean coal was then washed and dewatered by filtration. Afterwards they were dried, weighed and analysed for their ash content. The optimum operational parameters such as rotational speed and water flow rate for the KC were determined as 150 rpm and 2 l/min, respectively, for the medium and fine particle size groups.

1.3.1.4. Multi gravity separator (MGS)

A laboratory type of MGS called Mozley C900 with a length of 0.6 m and a diameter of 0.5 m was used throughout the experiments. A series of tests were conducted in order to determine the optimum working parameters given below for a maximum concentrate grade and a recovery when using the MGS (Table 5):

Table 5. *MGS experimental operating conditions*

Parameters	Values
Rotational speed (rpm)	230
Drum slope (°)	0, 2, 4
Wash water rate (l/min)	2, 3, 4
Pulp density (% w/w)	20
Feeding rate (l/min)	2
Shaking amplitude (mm)	15
Shaking frequency (cps)	4

Samples which were prepared to be in medium and fine particles sizes were fed to the inner surface of the equipment continuously. The heaviest particles were placed on the inner surface of the drum by infiltrating through the thin layer caused by the pulp under centrifugal forces. These were then transferred upwardly by the scrapers which rotate faster than the drum itself rotating in the same direction. The samples were reverse flow washed before they were discharged from the open end. The low density particles (coal) were transferred to the other exit behind the lower drum by the washing water. Consequently, the products were separately obtained after the steady-state conditions reached; they were then drained, dried, weighed and analysed to determine the optimum parameters given below:

The optimum conditions for medium sized material using MGS were determined as 2° and 2 l/min for the drum slope and feeding rate, respectively. On the other hand, the feeding rate for the fine sized material using MGS was determined as 4 l/min, when the drum slope was chosen as 0°.

1.3.2. Flotation methods

Coal is a solid matter having a heteropolar surface owing to the hydrophobic carbon structure and hydrophilic mineral matter content. Therefore, the flotation method has been used for the recovery of fine coal particles (hydrophobic part) for a long time. In this research, a Denver mechanical flotation cell which is commonly used worldwide and a Jameson Flotation Cell which is mainly used for the processing of fine coals were preferred. A series of flotation tests were conducted in order to float coal particles and to depress ash containing minerals under various operational parameters such as the dosages of collector, depressant and frothing agents. Flotation tests were carried out on the fine sized materials.

1.3.2.1. Mechanic flotation cell

A laboratory type of flotation cell with a capacity of 2 l and self-aerating character was used during the tests. Several tests were conducted to determine the optimum flotation parameters given below (Table 6):

Table 6. *Mechanical flotation cell experimental operating conditions*

Parameters	Values
Collector (kerosene) dosage (g/t)	7000, 8500, 10 000
Frother (AF65) dosage (ppm)	8, 16.5, 25
Depressant (Na_2SiO_3) dosage (g/t)	100, 550, 1000
Mixing rate (rpm)	1200
pH	Natural (7.3)
Pulp solid ratio (%)	10
Conditioning time (min)	8
Flotation time (min)	2

1.3.2.2. Experiments with the Jameson flotation cell

The Jameson Flotation cell, having a worldwide use of more than 250, has been successfully used for coal flotation, especially in Australia. The Jameson Cell whose operational parameters have been explained by various research, Jameson (Jameson, 1988), Sahbaz et al. (2008), was also chosen for this research under the given conditions (Table 7):

Table 7. *Jameson flotation cell experimental operating conditions*

Parameters	Values
Collector (kerosene) dosage (g/t)	700, 5900, 11 000
Frother (AF65) dosage (ppm)	8, 16.5, 25
Depressant (Na_2SiO_3) dosage (g/t)	100, 550, 1000
pH	Natural (7.3)
Pulp solid ratio (%)	5
Conditioning time (min)	8
Feeding rate (l/min)	12
Flow rate for washing water (l/min)	3.2
Tailing flow rate (l/min)	14.5
Bias factor rate	0.78
Air to pulp ratio	0.9
Cell (transparent plexiglas) diameter (d_H) (cm)	20
Vertical shaft (transparent plexiglas) diameter (d_D) and the length (L_C) (cm)	2 and 180
Nozzle (stainless casting steel) diameter (D_N) (cm)	0.4

2. Results and discussion

After the characterisation studies on the wastes of Number-4 pond, it can be said that increased ash content and decreased calorific value owing to the decrease in particle size is an expected result. Total sulphur content of the sample was increased up to the particle size of 0.106 mm, from which it decreased with a decrease in particle size. The reason why sulphur content is relatively lower at -0.038 mm is explained by the fact that sulphur is dominantly contained by the coal material (Table 2). In fact, when Table 1 and 2 is reviewed together, it is seen that total ash content and the loss of ignition values of the waste materials obtained from the elemental analysis show a good conformity. Likewise, total ash content of the waste materials is in good agreement with the ash values obtained from the elemental analysis. As seen from the characterization results, it can conveniently be said that materials under 0.038 mm should not be enriched because of its low carbon content while the other size groups could properly be enriched by using physical and physico-chemical methods.

Experimental parameters were also optimised by evaluating the results obtained from each tests on the various size groups. Ideal beneficiation curves were drawn using the results of combustible recovery and carbon content values experimentally obtained from the fine, medium and coarse size groups of the waste materials under the optimum conditions as well as using the theoretical results of the combined size groups concerned, comparisons were also made.

2.1. Enrichment tests on the coarse size group

The float-sink test results for the coarse size group is given in Figure 3. As seen from the ±0.1 density curve, it can be said that the washing process is made as “very easy”, “easy” and “difficult” at the densities of 1.8 gr/cm^3, 1.6-1.7 gr/cm^3 and at <1.6 gr/cm^3, respectively. A clean coal was obtained with an ash content of 15%, by weight of 88% and a recovery rate of 96.4%, using the optimum density of 1.7 gr/cm^3.

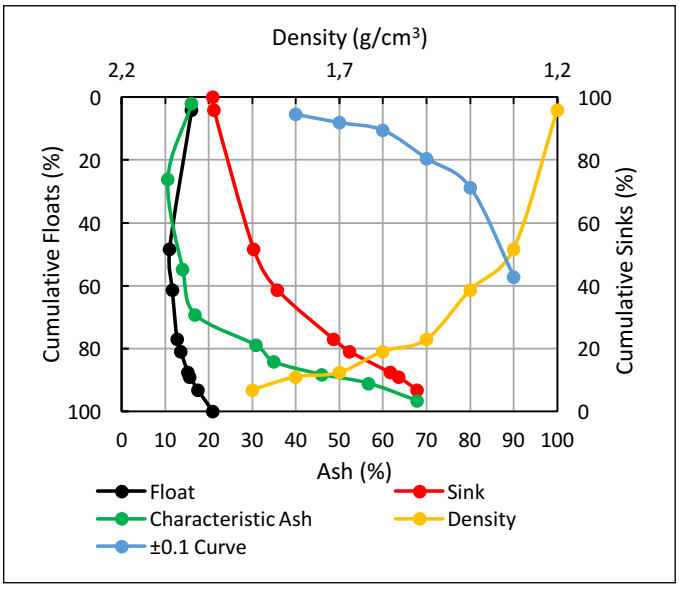

Figure 3. *Float-Sink test results for the coarse particles*

2.2. Enrichment tests on the medium size group

Four different methods were used in order to enrich waste coals in the medium size group (ash content is 31.13%) which are namely; classification, classification + Spiral, MGS and KC. Recovery performance curves obtained from the results are given in Figure 4.

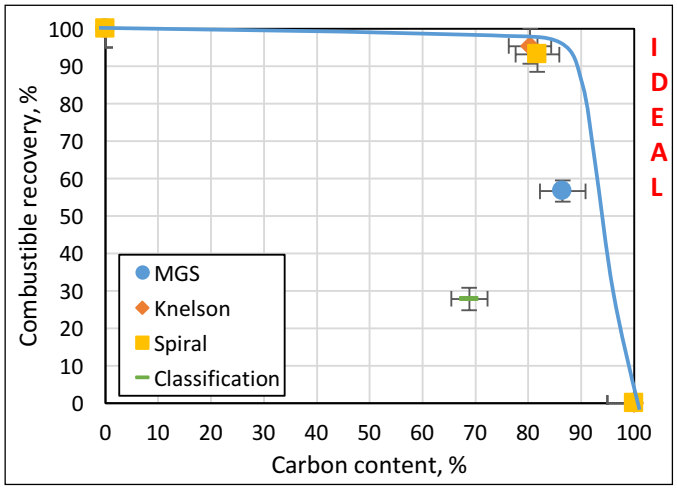

Figure 4. *Comparisons for the recovery performances of various gravity methods on the medium size group*

The best results were obtained by using Spiral and KC at optimum conditions with regard to the carbon content and combustible recovery results, while carbon content of the clean coal produced by classification was found to be 68.87%. The best combustible recovery value was obtained as 95.29% when using the KC; the carbon content was found to be 80.37% in these tests. On the other hand, the best carbon content value was reached by MGS as approximately 85%. However, the combustible recovery could only reach a value of 55% by MGS.

Similar carbon values were obtained (~34% ash) by Altun et al. (2010) and Erdem, et al. (2012) from the beneficiation tests on waste coals using MGS. However, combustible recovery values were relatively higher than those of this research. Aslan (2007), reached a clean coal with a combustible recovery of 60% and an ash content of 36.1% in his research. In all these beneficiation tests using waste coals and MGS, both combustible recovery and ash content values were found to be high. However, high combustible recovery values were obtained together with relatively lower ash contents in this research.

As seen from Figure 4, a clean coal with an ash content of 81.73% was obtained with a combustible recovery of 81.73% by using Spiral. In research done by Sivrikaya (2014), a clean coal with a similar ash content was obtained by a combustible recovery of 57% on coals at -1.5 mm particle size.

2.3. Enrichment tests on the fine size group

The flotation method was also used together with physical methods for the beneficiation of fine sized waste coals. The results of optimum combustible recovery and carbon content obtained by using the classification method and other beneficiation methods after classification are summarized in Figure 5.

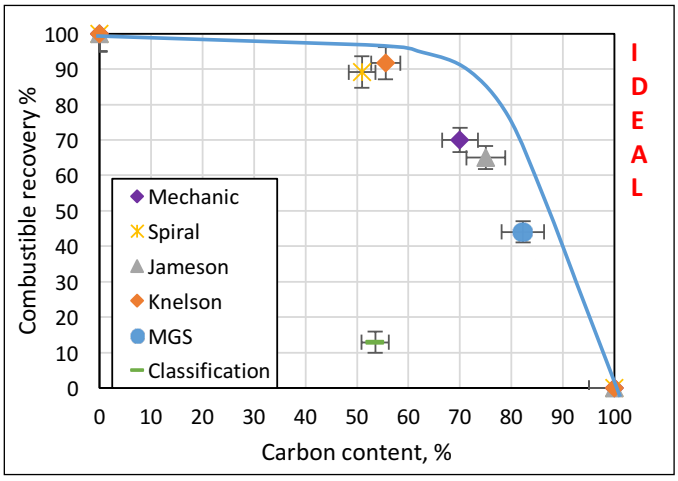

Figure 5. *Performance comparisons for the methods used in the beneficiation of the fine sized group*

A clean coal with a carbon content of 50.8% was obtained by a combustible recovery of 12.9% when the classification method was used on the fine size group. It is well known that methods with higher recovery performances such as MGS, KC and Flotation have become more important for the beneficiation of fine waste coals. As a matter of fact, the highest recoveries were obtained by using Spiral and KC for the fine sized coals as well as for the medium size group. Combustible recoveries of 89.12% and 91.66% were obtained when Spiral and KC were used, respectively. However, carbon contents still remained low with these equipment (around 55%).

The highest carbon content (82.24%) was obtained by MGS in this group of tests. From the tests, it was realised that MGS was more selective but the recovery rate was still low with MGS. In fact, Falconer (2003) reported that MGS provided better selection for fine size groups (75~10 micron). Moreover, similar results were obtained by Ozgen et al. (2011) and Sabah et al. (2007) in their research they achieved clean coals with 20-23% ash contents from the waste of Tunçbilek/Kütahya washery by combustible recoveries of 50-55%. Sonmez and Koca (1997) also gained clean coals with an ash content of 17.62% from the wastes of Tunçbilek/Ömerler washery (41% ash content) by a combustible recovery of 70.66%. In a research done by Koca et al. (2000), a clean coal with an ash content of 17.39 and a lower calorific value of 5082 kcal/kg was obtained by a combustible recovery of 63.08% using MGS from the wastes of Alpagut-Dodurga washery whose ash content, total sulphur and lower caloric values were originally 49.19%, 1.37% and 2650 kcal/kg, respectively. It could properly be concluded that several researches have been carried out on the bene-

ficiation of waste coals using MGS and the results of those studies show similarity with the results of this research.

Meaningful results for carbon content and combustible recovery were not obtained by using the two different types of flotation equipment on the fine size group. In other words, clean coals were obtained with carbon contents of 70% and 75% and combustible recoveries of 70% and 65% from the mechanical flotation and Jameson floatation tests, respectively (Figure 5).

The result can be explained by the oxidation of coal and also by the fact that oxidation process can alter the properties of the coal surface and coal structures. It is well known that low rank coals and oxidised coal surfaces are difficult to float and they require excessive use of kerosene since high oxygen containing functional groups on coal surface cause coal surfaces to become even further hydrophilic (Bunt, 1997; Piñeres et al., 2018; Polat et al., 2003; Sivrikaya, 2014; Sokolović et al., 2012; Tao et al., 2002; Wang and Tao 2018; Xia et al., 2017). Tao et al. (2002) reported that they obtained relatively better results from the mechanical floatation tests using special reactive agents on the oxidised waste coal, however, they were not able to gain successful results from the column floatation tests.

During the optimisation tests, it was found that each size group required different beneficiation methods for better results. Figure 6 summarises the performances of each method used for the size groups used. As seen from Figure 6, spirals become more advantageous with key properties such as being economical, simple and solid (requiring less maintenance and having no movable part) as well as they do not demand chemical use while processing. Almost ideal values were obtained in the medium size group, however, the results for carbon content could not be regarded as ideal in the fine size group. This result was explained by the fact that fine clay particles were mixed up with coal particles through secondary flows when testing with the fine size group. Therefore, equipment such as MGS which applies higher centrifugal forces, should be more meaningful for fine size groups. It was also realised that better results could be gained if the secondary beneficiation process was applied by reducing the solid ratio and water flow rate after preliminary beneficiation by the spiral.

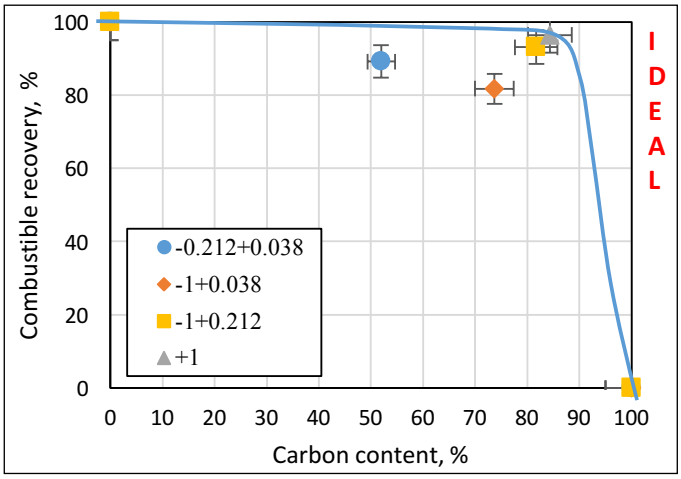

Figure 6. *Comparison of the beneficiation methods used on the various particle size groups*

Centrifugal separators such as KC and MGS concentrators still have limited industrial use although they have been developed for the beneficiation of finely sized coals or minerals. From the test results, it can also be concluded that spirals are good at medium size groups, however, MGS concentrators should be used for fine sized coals to obtain higher carbon content; and KC should be preferred for higher combustible recoveries. The Jameson flotation cell can also be considered for fine sized coals. However, the flotation method should be taken into account only for fresh waste coals which means that it should be used before oxidation occurs to get higher performances.

Conclusion

This research was carried out to determine enrichment possibilities for fine waste coals of WLC by using various physical and physico-chemical methods. The other purpose of the research was to provide a sustainable solution for the environmental problems caused by the deposition of these wastes and to compare the results of various methods for the beneficiation of such waste coals with different size fractions. During the investigation, various physical processing equipment such as sink-float tank, spiral separator, KC, MGS and equipment using physico-chemical methods such as a mechanical cell and the Jameson cell were used.

From the tests carried out, a clean coal with a carbon content and a combustible recovery of 85% and 97% were obtained, respectively, when sink-float method and coarse particle size group (+1 mm) were chosen. Therefore, it was concluded that there was no other equipment needed for the beneficiation of this size group. From the tests with the medium particle size group (-1+0.212 mm) using spiral and KC, combustible recovery of up to 94% was reached together with a carbon content of 81%. A carbon content of 86.49% with a low combustible recovery of 56.58% was obtained by using MGS. In the fine particle size group (-0.212+0.038 mm), the highest combustible recovery values were obtained by using spiral and KC (approximately 90%). Almost ideal carbon content was reached as 82.24% when MGS was used. In the flotation tests, however, a clean coal with carbon contents of 70-75% was obtained through a combustible recovery of 70% by using both mechanical and Jameson Cells.

From the tests results obtained, it was understood that Spirals could efficiently be used for the processing of coal slimes in order to prevent environmental problems and economic loses. The use of MGS, on the other hand, could also be considered as an alternative to spirals whose selectivity is relatively reduced in fine particle sizes. However, more experiments are needed to investigate the reasons of low combustible recovery they produce. Moreover, flotation methods should be considered as an alternative owing to its moderate high carbon content and combustible recovery values over 70%, especially in fine particle size groups. It was also found that the Jameson flotation cell had better selectivity over the mechanical cell and, therefore, it possesses a potential of producing higher carbon content and combustible recovery values on non-oxidised coal surfaces.

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Original Research

Recovery of chromite from concentrator plant tailings

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A B S T R A C T

In this study, experimental studies have performed to recover chromite from Eskiköy-Sivas chromite concentrator which is owned Bilfer Madencilik ve Turizm A.Ş. Mineralogical and liberation measurement studies were performed, and it was decided to grind the feed to 100% finer than 300 µm.

Gravity concentration and wet high intensity magnetic separation (WHIMS) tests were performed. After grinding to -300 µm, -38 µm fraction which cannot be recovered efficiently was removed. The studies were conducted on 300+100 µm and -100+38 µm fractions. After the beneficiation tests, it was determined a circuit consists of spiral concentrator and shaking tables could produce a concentrate containing 48% Cr_2O_3 from the tailings having 6.54 % Cr_2O_3, with a 56% recovery.

Keywords: *Tailings, Particle Size Distribution, Spiral, Shaking Table, Magnetic Separation.*

Introduction

Chromite ($(Mg,Fe^{+2})(Cr,Al,Fe^{+3})_2O_4$), which has been used metallurgy, chemical, refractory and foundry industries, is an irreplaceable mineral.

Türkiye is the fourth in the chromite reserves and second in the production (USGS, 2022). Chromite deposits are distributed to all regions. Since the beneficiation plants have been in operation since the beginning of the 20th century, there are large amount of tailings accumulated containing varying amount of chromite, and the depletion of high grade deposits have been motivated the researchers for the recovery of chromite from old tailings (Acar, et al.,2018, Güney, et al., 2016, Güney, et al., 2001 and Çiçek, et al. 2002).

Currently, there are two operating plants in Türkiye processing tailings.

In countries such as South Africa, Iran, and India, which have a significant share in chromite production, there are studies to obtain concentrate from tailings. (Tripathy et al, 2011, Khakmardan et al, 2020, Feng and Aldrich, 2003, Tripathy et al, 2013 and Kumar et al, 2009).

It is possible to enrich the chromite ore by different methods. However, it is necessary to choose the most appropriate and economical management. In the selection of the most suitable method, mineralogical, physical, and chemical properties of the ore have an important place. (Deniz et al., 2001)

Gravity concentration has been the main method used in chromite beneficiation. Dense medium separation, jigging, spiral concentrators, shaking tables and Multi-Gravity Separator are used in operating plants (Burt, 1984).

Magnetic separation and flotation have also found application in a few cases (Nafziger, 1975). As the chemical composition and attenuation grain size of chromite, which has a spinel structure, are very variable, enrichment methods naturally also contain differences. For example, increased the Fe^{+2} ratio in the chromite content increases its magnetic susceptibility. Therefore, it can be enriched by high-intensity magnetic separation. (URL-1)

Beneficiation of chromite from tailings is more difficult and complex since free liberated chromite particles were already recovered in the original process.

This paper was extracted from MSc thesis of Mehmet Özyurt at Sivas Cumhuriyet University and presents beneficiation studies have been performed for the recovery of chromite from the tailings of a chromite beneficiation plant operating since 1987 in Eskiköy- Sivas.

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1. Materials and methods

1.1. Sampling

Samples were taken from the tailing storage facility of the mine by trenching and shaft samples in both vertical and horizontal axes. Main sample was then divided to sub sample of 500 kg by coning-quartering.

1.2. Characterization of the sample

1.2.1. Chemical composition of the sample

XRF method was used for chemical analyses. The chemical composition of the sample is given in Table 1.

Table 1. *Chemical composition of the tailings*

% Amount							
Cr_2O_3	Fe_2O_3	Al_2O_3	MgO	SiO_2	CaO	Ni	Co
6.54	6.34	2.12	35.05	28.13	1.12	0.28	0.02

1.2.2. Size distribution of the tailings and Cr_2O_3 distribution of the fractions

The size distribution of the tailings after wet sieving and Cr_2O_3 content of the size fractions are given in Table 2.

Table 2. *Size distribution and Cr_2O_3 content of the size fractions.*

Sieve Size (mm)	Weight (%)	Cr_2O_3 %	Distribution (%)
-9.50+1.18	4.85	2.65	2.01
-1.18+0.6	14.71	4.33	9.95
-0.6+0.3	21.42	5.25	17.57
-0.3+0.106	25.08	6.36	24.91
-0.106+0.038	14.06	10.04	22.06
-0.038+0.025	3.24	16.65	8.41
-0.025	16.64	5.81	15.10
Total	100.00	6.40	100.00
Assay	-	6.54	-

As can be seen from the Table 2, chromite content of the size fractions increases as the size decreases down to 25µm. About 23 % of Cr_2O_3 is in the -38 µm, while 30% of it is in +300µm.

1.2.3. Determination of Mineral Composition and Liberation

1.2.3.1. Quantitative XRD Analysis

XRD pattern of the sample were obtained by using Rigaku-Miniflex 600 equipment. XRD pattern of the tailing sample is given in Figure 1 and its mineral composition is given in Table 3.

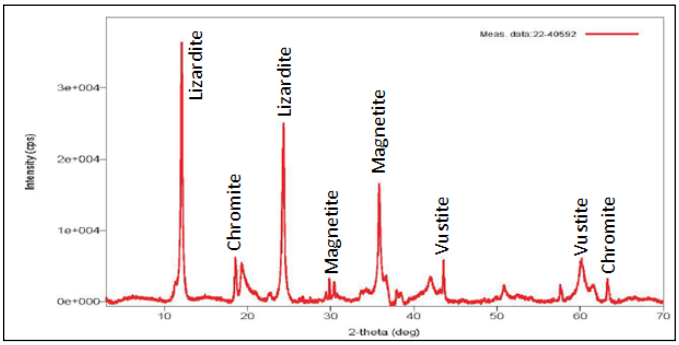

Figure 1. *X-ray diffraction pattern of the tailing*

Table 3. *Mineral composition of tailing as measured by quantitative XRD*

Mineral	Mineral Formula	Weight (%)
Lizardite	$Mg_3 (Si O_5) (O H)_4$	84.5
Magnetite	$Fe_3 O_4$	2.2
Wustite	$Fe._{9712} O$	3.6
Chromite	$FeO Cr_2 O_3$	4.7
Amorphous solid	-	5.0
Total	-	100.0

1.2.3.2. Determination of liberation

Grain counting using an optical microscope is one of the methods that can be applied to determine the degree of attenuation. It is based on the principle of examining the product remaining on each sieve in the sieve series with a microscope after the sieve analysis is done as a result of the size reduction processes.

Easily identifiable grains can be counted in "Stereo (Binocular) Microscopes" up to 75 µm. The method is based on counting the precious and non-precious free particles and the combined particles under the microscope.

For the determination of liberation degree of the tailings particle counting under binocular microscope. For this purpose, -300+212 µm, -212+150 µm, -150+106 µm and -106+75 µm, size fractions were prepared by wet sieving.

Liberation degrees of the size fractions are given in Figure 2. As expected, the liberation increases as the size decreases. The liberation of the finest fraction studied, -106+75 µm, was found to be 76.52% which denotes grinding would be required before beneficiation. Herefore, the sample was ground to 100% finer than -300 µm.

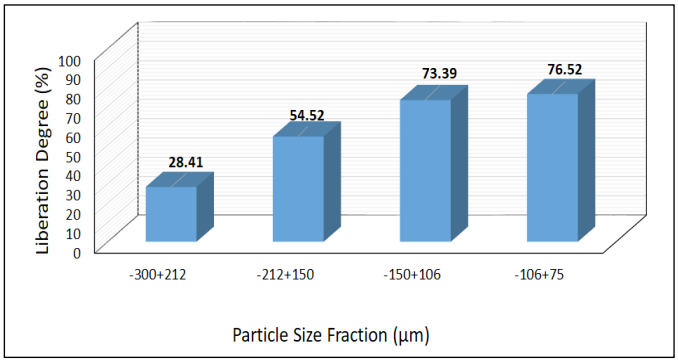

Figure 2. *Liberation degree of size fractions*

1.3. Mineralogy and liberation of ore produced from quarries

The bright sections of the hand samples taken from the quarries that provide raw materials to the ore beneficiation plant, prepared by embedding in araldite, were examined by ore microscope. Serpentine mineral containing euhedral and semi-euhedral chromite crystals and olivine residues filling them were observed in these sections. Most of the chromite crystals had dimensions of 0.25-0.3 mm. Chromite texture is generally in cataclastic structure and not strictly angular. Cataclastic tissue is a structure prone to slime production. It is possible to release the chromite to a large extent as a result of grinding the ore below 300 microns.

It was determined that the data obtained from the determination of the degree of attenuation of the waste and the data of the attenuation dimension obtained from the microscopic analysis of the run-of-the-mill ore were consistent.

1.4. Beneficiation Studies

Since the amount of tailings is about 500 kg, it was logical to build the tailing recovery circuit in the existing concentrator building. Therefore, to reduce the footprint of the circuit, spiral concentrator was thought to be the most convenient alternative as a pre-concentration step. On the other hand, the efficiency of gravity concentration drops sharply for the particles smaller than 40µm. Multi Gravity Separator has higher efficiency than shaking tables for this size range was not considered due to the very high investment cost of the equipment. Instead, -38 µm was removed from the feed by wet screening. The fractions prepared and their Cr_2O_3 contents are given in Table 4.

Table 4. *Cr_2O_3 contents of size fractions used in tests*

Size (micron)	Weight %	Cr_2O_3 %	Distribution (%)
-300+100	65.28	6.46	63.99
-100+38	20.14	8.12	24.81
-38	14.58	5.06	11.20
Total	100.00	6.59	100.00
Analysis		6.54	

The simplified flowsheet for the beneficiation studies is given in Figure 3.

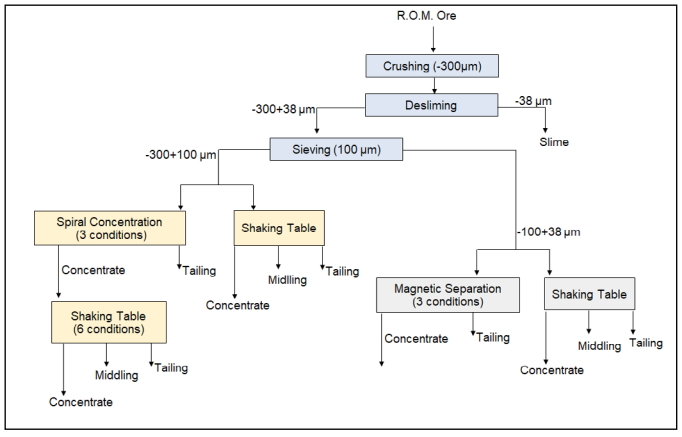

Figure 3. Simplified flowsheet of beneficiation studies

1.4.1. Spiral Beneficiation Studies for -300+100 µm Fractions

The spiral concentrator used in the tests has 600mm diameter, seven turns (Mineral Deposit A87D). The test conditions are given in Table 5.

Table 5. *Spiral test conditions*

Parameter	Value
Feed Size (µm)	-300+100
Solid Content (%)	30
Flowrate (m^3/s)	2
Product Splitter Position	
S1	High grade
S2	Concentrate + Middling
S3	High Yield (Pre-concentrate)

1.4.2. Shaking Table Tests for -300+100 µm Fraction

The dimension of the shaking table test is 500x1.200 mm (Wilfey). The shaking table was fed with the help of a vibrating feeder placed under a 5 kg capacity bunker. Then, the tests were carried out by adjusting the washing water and the table at optimum values. The test conditions are given in Table 6.

Table 6. *Shaking table test conditions*

Variable	Value
Feed Size (µm)	-300+100
Solid Content (%)	30
Feed Flowrate (m^3/h)	0.05
Wash Water (l/min.)	10
Table Tilt (degrees)	4

1.4.3. Shaking Table Test for -100+38 µm Fraction

The test conditions for -100+38 fraction shaking table test are given in Table 7.

Table 7. *Shaking table test conditions*

Variable	Value
Feed Size (µm)	-100+38
Solid Content (%)	25
Feed Flowrate (m^3/h)	0.04
Wash Water (l/min.)	6
Table Tilt (degrees)	3

1.4.4. WHIMS Tests

These tests were performed with -100+38 µm.

Chromite displays paramagnetic properties, and its susceptibility varies according to the substituting elements in the crystal structure (Svoboda, 1987).

Matrix type WHIMS (Carpco) was used in the tests as described in the literature (Carpenter, 1964 and Svoboda, 1987).

After the pulp having 25% solids onto the matrix, the feeding was stopped 5 litres of wash water was used to wash out non-magnetics. Steel balls was used as matrix material. The tests were performed at 0.49, 0.86 and 1.10 Tesla magnetic field intensity.

2. Results and discussion

2.1. Spiral Tests

The test results for three different product splitter positions, S1, S2 and S3, are given in Table 8, 9 and 10, respectively. The effect of splitter position on the weight recovery, the grade and the recovery are shown in Figure 4.

Table 8. *Spiral concentration test results (splitter position S1)*

	S1		
	Weight %	Cr_2O_3 %	Recovery %
Concentrate	6.16	24.90	22.70
Tailing	93.84	5.57	77.30
Feed	100.00	6.76	100.00

Table 9. *Spiral concentration test results (splitter position S2)*

	S2		
	Weight %	Cr_2O_3 %	Recovery %
Concentrate	12.03	21.33	36.79
Tailing	87.97	5.01	63.21
Feed	100.00	6.97	100.00

Table 10. *Spiral concentration test results (splitter position S3)*

	S3		
	Weight %	Cr_2O_3 %	Recovery %
Concentrate	25.11	14.20	56.21
Tailing	74.89	3.71	43.79
Feed	100.00	6.34	100.00

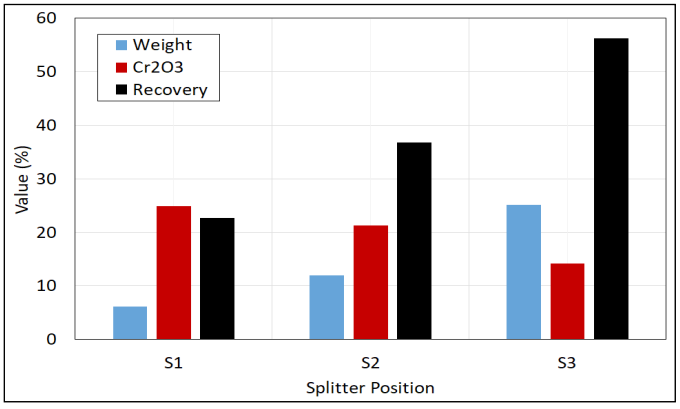

Figure 4. *Effect of splitter position on concentrate weight, Cr_2O_3 grade and recovery*

As can be seen from Table 10, even for the largest splitter position, the recovery was 56.2%. However, 75% of the feed was removed as tailings. Pre-concentration with spiral concentration would reduce the number of shaking tables required significantly and allows to fit in existing concentrator building.

2.1.1. Shaking Table Test with Spiral Concentrate

Using the spiral concentrate taken at the largest splitter position (S3), a shaking table test was performed, and the results are presented in Table 11.

Table 11. *Shaking table test results with spiral pre-concentrate*

	Weight %	Cr_2O_3 %	Recovery %
Concentrate	25.55	47.51	77.89
Middling	30.17	7.88	15.26
Tailing	44.28	2.41	6.85
Feed	100.00	15.58	100.00

The results showed that a concentrate having 47.51% Cr_2O_3 with a stage recovery of 77.89 % could be obtained. Middling taken at this stage could be recycled to the feed to increase the recovery.

2.2. Shaking Table Test Results

2.2.1. -300+100 µm Size Fraction

Shaking table test for -300+100 µm fraction is given in Table 12.

Table 12. *Shaking table test results with R.O.M. ore*

	Weight %	Cr_2O_3 %	Recovery %
Concentrate	7.82	50.83	57.62
Middling	1.70	37.28	9.18
Tailing	90.49	2.53	33.20
Feed	100.00	6.90	100.00

Shaking table enables the production of concentrate having over 48% Cr_2O_3 with a higher recovery than spiral concentrator.

In a plant application, a scavenger stage must be added to the spiral concentration to increase the recovery. Then rougher-scavenger concentrate can be fed the shaking tables for final upgrading. Otherwise, the performance of shaking table is superior comparing the spiral concentrator in single stage.

2.2.2. -100+38 µm Size Fraction

The test results are given in Table 13.

Table 13. *Shaking Table Test Results with -100+38 µm size fraction*

	Weight %	Cr_2O_3 %	Recovery %
Concentrate	1.73	42.34	8.72
Middling	14.03	25.76	43.02
Tailing	84.24	4.81	48.26
Feed (Analysis)	100.00	8.40	100.00

As it can be seen from Table 13, both the grade and the recovery are low in single stage beneficiation. Since 25% of the chromite is in -100+38 µm fraction, it must be processed. To increase the performance of the shaking table, two stage separation may be used. In the first stage, a combined product of concentrate and middling can take while 80-85% of the material could be removed as tailings. In the second stage, a concentrate can be taken and middling could be recycled back to the feed of the second stage. Such an arrangement would improve both the recovery and the grade.

2.3. WHIMS Results

The results of the WHIMS test at 0.49, 0.86 and 1.10 Tesla are given in Table 14, 15 and 16, respectively. The results are also presented for different field intensities in Figure 5.

Table 14. *H.I.W.M.S test results with -100+38 µm fraction (0.49 Tesla)*

	0,49 Tesla		
	Weight %	Cr_2O_3 %	Recovery %
Concentrate	60.90	12.27	91.92
Tailing	39.10	1.68	8.08
Feed	100.00	8.13	100.00

Table 15. *H.I.W.M.S test results with -100+38 µm fraction (0.86 Tesla)*

	0,86 Tesla		
	Weight %	Cr_2O_3 %	Recovery %
Concentrate	78.13	10.14	97.16
Tailing	21.87	1.06	2.84
Feed	100.00	8.15	100.00

Table 16. *H.I.W.M.S test results with -100+38 µm fraction (1,10 Tesla)*

	1,10 Tesla		
	Weight %	Cr_2O_3 %	Recovery %
Concentrate	89.46	9.03	99.25
Tailing	10.54	0.58	0.75
Feed	100.00	8.14	100.00

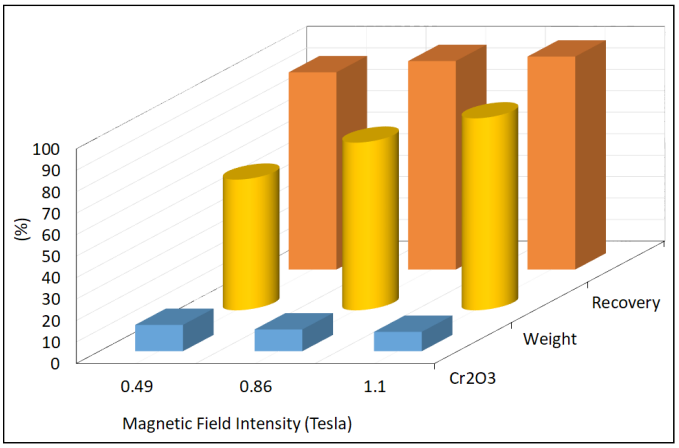

Figure 5. *Effect of magnetic field intensity on concentrate weight, grade, and recovery*

The best result was obtained at 0.49 Tesla field intensity. The tailing grade was 1,68% Cr_2O_3 and 40% of the material could be with 8% metal loss.

In larger plants, WHIMS could be used an efficient pre-concentration step for this fraction since single WHIMS equipment could process 300 tph. This could reduce the number of equipment used in downstream processing.

The chromite recovery in conventional plants is higher at the medium size range and deteriorates both at the coarser and the fine size range. The losses at the coarser range are usually result from poor liberation, the efficiency of shaking tables and spirals are lower for the finer size range.

There is an operating plant processing Üçköprü- Fethiye chromite concentrator tailings. The plant uses shaking tables and MGS for chromite recovery. MGS is particularly useful for the recovery of fines (-100µm) fraction which consists of 80% of the Cr_2O_3. Over 2 million tons of tailings was processed (Uysal, 2022).

As the high grade and easy to process ores were almost depleted, the lower grade ores are now being processed. This requires increase in plant capacities to keep the operation profitable. With this respect, spiral concentrators have been found applications in high-capacity plants (Burt, 1984). Modern spirals can process 12-18 tph feed in a 1 m^2 footprint. Such a capacity can be processed 4-6 triple-deck shaking tables each requires ~10 m^2. Although the efficiency of shaking tables is higher than spiral concentrator in single stage separation, the investment, operating costs, control, and water consumption would be in favour of spiral concentrator.

The best arrangement for a general flowsheet may be removal of barren oversize, grinding, pre-concentration by spirals, final concentration by shaking tables and MGS for fine fraction.

Considering the limited amount of tailings in Eskiköy plant, two stage spiral concentration (rougher-scavenger) and the shaking tables for final concentration was found to be feasible and could be installed in the existing concentrator building.

Conclusions

Since the chromite are locked with gangue minerals at the sizes coarser than 300 µm, the tailings should be ground to 100% finer than 300 µm before beneficiation.

Spiral concentration tests showed that 75% of the feed could be removed with a 43,79 % Cr_2O_3 loss. To increase the recovery, a scavenger stage is recommended.

WHIMS could be used as an efficient pre-concentration step for -100+38 µm fraction.

Feasibility studies showed that the tailings of Eskiköy plant can be processed economically with a minimum investment by using two stage spirals and shaking tables.

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Original Research

Modelling of the flotation process by central composite design for obtaining superior grade feldspar

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A B S T R A C T

Feldspar is usually found in conjunction with titanium and iron minerals. Feldspar should be separated from other minerals by generally magnetic separation or/and flotation with high grade. However, due to the similarities in the properties, feldspars are difficult to separate from gangue minerals by flotation.

In this study, the degradability of iron was investigated by mica flotation, and Central Composite Design (CCD) was used to plan and analyze the results. During the study, the effect of pulp density, pH, collector amount and air flow rate on the iron grade and the recovery of the obtained feldspar concentrate were modelled. Then, estimation of the optimum conditions and verification tests were performed. The iron content was reduced to 0.14% by mica flotation. However, this reduction amount was found to be insufficient. Finally, iron content was reduced to 0.05%. Considering that the maximum iron content of the superior grade feldspar is 0.1%, it can be said that two stage flotation is successful without different processes such as magnetic separation.

Keywords: *Feldspar flotation, superior grade feldspar, central composite design, modelling of the mica flotation.*

Introduction

The feldspar which constitutes approximately 60-65% of the earth's crust has a wide range of use, mainly in the ceramic and glass industries. Turkey has 14% of the world feldspar reserves and as of 2016, the 5.5 million tons of feldspar export has been an important part of the country's economy with an income of 155.5 million dollars (Sahiner, 2017). The usability and market price of feldspar are strongly related to presence of the impurities such as rutile and ilmenite which contain the colorant Fe_2O_3 and TiO_2. In the world, the most common methods employed in the enrichment of feldspar are magnetic separation and flotation. In Turkey, feldspar is generally enriched by flotation method in industrial scale.

Celik et al. (Celik et al, 2001) tried to remove the colorant impurities by a combination of magnetic separation and flotation methods. In this study, magnetic separation was used both before and after flotation. It was found that magnetic separation after flotation produced superior grade feldspar concentrate. In the study of Seyrankaya in 2003 (Seyrankaya, 2003), obtaining albit concentrate which is suitable for ceramic and glass industries was investigated by using two-stage flotation method from Albit ore in Muğla-Milas region. In a study published in 2006 by Orhan and Bayraktar (Orhan and Bayraktar, 2006), for the flotation of mica and metal-oxides from Milas Cine feldspars, they examined the interaction of the amines that remained after the first stage mica flotation with the sodium oleate used in the second stage flotation. According to the results obtained, with dewatering and washing applied after the first stage, the yield was increased to 94.58% from 86.67% in case of no washing. Heyes et al. (Heyes et al, 2012) published a review about removing minerals such as quartz, mica, ilmenite, rutile and magnetite from feldspar by flotation. The feldspar flotation in this article was explained as three stages flotation; in first stage, micas were floated with amines, in the second stage, titanium and iron-oxide minerals were floated with anionic collectors, and in the last stage the feldspar that activated by fluorite ions were floated with amines and leaving quartz in tailing. In a study published in 2016, Larsen and Kleiv (Larsen and Kleiv, 2016) indicated that quartz could be separated from feldspar by flotation with highly selective and high yields with dilute HF. In another study of the same researchers (Larsen and Kleiv, 2017), they stated that quartz yield depends on the conditioning time with HF, the type of frother and the concentration

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of HF and frother. In the study published by Jia Tian et al. (Tian et al, 2017), it was determined that the mixture of dioxylammonium chloride as a cationic collector and sodium oleate as an anionic collector showed high selectivity in the separation of spodumene from feldspar. Surface tension measurements, adsorption measurements, zeta potential measurements and FTIR analysis were carried out to determine the adsorption mechanism. In 2018, the same research team (Wu et al, 2018) published a study about spodumene-feldspar flotation with the use of the cationic reactant with the anionic collector. Due to the attachment mechanism, feldspar flotation was reported to be improved as the particle size decreased by Longhua Xu et al. (Xu et al, 2017). Again, in 2018, the same researchers published another study comparing the different flow diagrams for the spodumene flotation performance and recycling of mica and feldspar from the lithium wastes (Tian et al, 2018).

In a study published by Gulgonul and Celik in 2018 (Gulgonul and Celik, 2018), the selective flotation of Na-K (albite-microcline) feldspar flotation in the presence of K^+ ions as the potential-determining ion was investigated. In Brazil as one of the most important granite slab producers, quartz and iron removal from granite wastes studies were done (Silva et al, 2019). In this study, iron was reduced from 3.2% to 0.48% by magnetic separation. In another study published in 2018 (Sulaymonova et al, 2018), magnetic separation as a physical method, chemical enrichment using HCl+H_2SiF_6 mixture reagents and flotation with a specially designed flotation cell were used for quartz separation. In a published review, it was stated that crystalline structure, monovalent salts, flotation reagents and particle size distribution are important factors in the process. Also, mixed collectors are given as a promising method for feldspar flotation (Zhang et al, 2018).

Statistical design methods which allow effective analysis of effective parameters with less experimentation have been used for many years. For example, in a study published by Aytar et al. (Aytar et al, 2014), the Taguchi methodology, a statistical design method, was used in the optimization of the process in the fungal desulphurization study. The usage of these methods especially in academic studies has been increased with the use of response surface methods (RSM) that define effective parameters better and enable the process to be mathematically modelled (Aksoy and Sagol, 2016; Oluklulu and Koca, 2018). As an example, the study of Koca et al. (Koca et al, 2017) can be given. In this study, Box Behnken Design (BBD) which is a RSM method was used to investigate microbial treatment and flotation of lignites. Another common RSM method in the literature is Central Composite Design (CCD). When these two response surface methods are compared, BBD method has a significant disadvantageous compared to CCD. The main disadvantage of BBD method is that it requires less experiments at low (-1) and high (+1) levels. Therefore, it generally decreases the success of the predictions of these regions during the optimization stage (Croarkin and Tobias, 2015). In the literature, CCD has been used in experimental studies on many different topics including modelling and optimization in the literature, such as the calibration criteria optimization of gas flowmeters (Guerra et al, 2018), optimization and the desirability function for sorption of methylene blue from aqueous solution (Sadhukhan et al, 2016) etc. As in all experimental studies, CCD has been utilized in mining and mineral processing as well, such as coal preparation (Aksoy and Sagol, 2016; Aslan, 2007), pyrolysis (Onay and Koca, 2019), gold-silver recovery in cyanidation process (Karimi et al, 2010), copper leaching from refractory flotation tailings (Bai et al, 2018), optimizing of sphalarite flotation (Mehrabani et al, 2010).

In this study, the cleanability of feldspar in Aydın Söke region by mica flotation was investigated. The studied sample contains 0.24% Fe. In the case of superior grade feldspar, it is required by the ceramic factories that the iron content should be below 0.1% Fe. The aim of this study was originally to reduce the iron content with mica flotation and statistical experimental design was used to plan flotation experiments and to analyze the results. However, according to results of mica flotation, the iron content was not found to be sufficient. Therefore, a series of iron oxide flotations was needed to reduce the iron content to less than 0.1% in order to obtain superior grade feldspar.

1. Materials and Method

1.1. Materials

Feldspar samples were taken from Aydin Soke region. The feldspar ore found in this region is also used extensively in the ceramic industry established in that region. The sale price of these Feldspars is inversely proportioned to the iron content of the ore. Therefore, it is aimed to reduce Fe content to less than 0.1% with the highest feldspar yield. Microscope studies showed that the mica and other impurities contained in the ore were in the liberated state at -0.1 mm. Chemical analyzes of the samples by XRF are given in Table 1. Due to the low rate of impurities in the ore, it was not possible to determine the minerals contained as impurity in the feeding sample. Therefore, for the determination of unwanted minerals, XRD and SEM-EDS analyzes were carried out on the floating products obtained from reverse flotations. One of the results of SEM-EDS is given in Figure 1 as an example. All analyses, XRF, XRD and SEM-EDS, were repeated three times and mean results were presented in the manuscript.

Table 1. *Chemical analysis of feldspar sample (XRF analysis).*

Content	%	Content	%	Content	%	Content	%
Al_2O_3	17.70	Cu	<0.002	Ni	0.002	TiO2	0.29
As	<0.002	Fe	0.24	P	0.148	V	<0.002
Ba	0.051	K_2O	3.36	Pb	0.016	Zn	0.002
CaO	0.58	MgO	0.16	S	0.003	Zr	0.020
Co	0.002	MnO	<0.01	SiO_2	70.00	LOI*	0.4
Cr	<0.001	Na_2O	7.43	Sr	0.013		

*Lost of ignition

According to XRD and SEM-EDS analysis, both sodium (albite) and calcium (anorthite) structure ($NaAlSi_3O_8$-$CaAl_2Si_2O_8$ (triclinic)) were determined in the ore. In addition, alkali feldspar (XAl(1-2)Si(3-2)O(8) X: Na, K or Ca) were observed, and quartz was also found as silicate mineral. In the analysis of the floated product of mica flotation, muscovite was determined as a mica mineral and also kaolin minerals were detected. In the floating product obtained from iron flotation, chlorite mineral was found as an iron-containing mineral. Again, the presence of apatite was found in the same product.

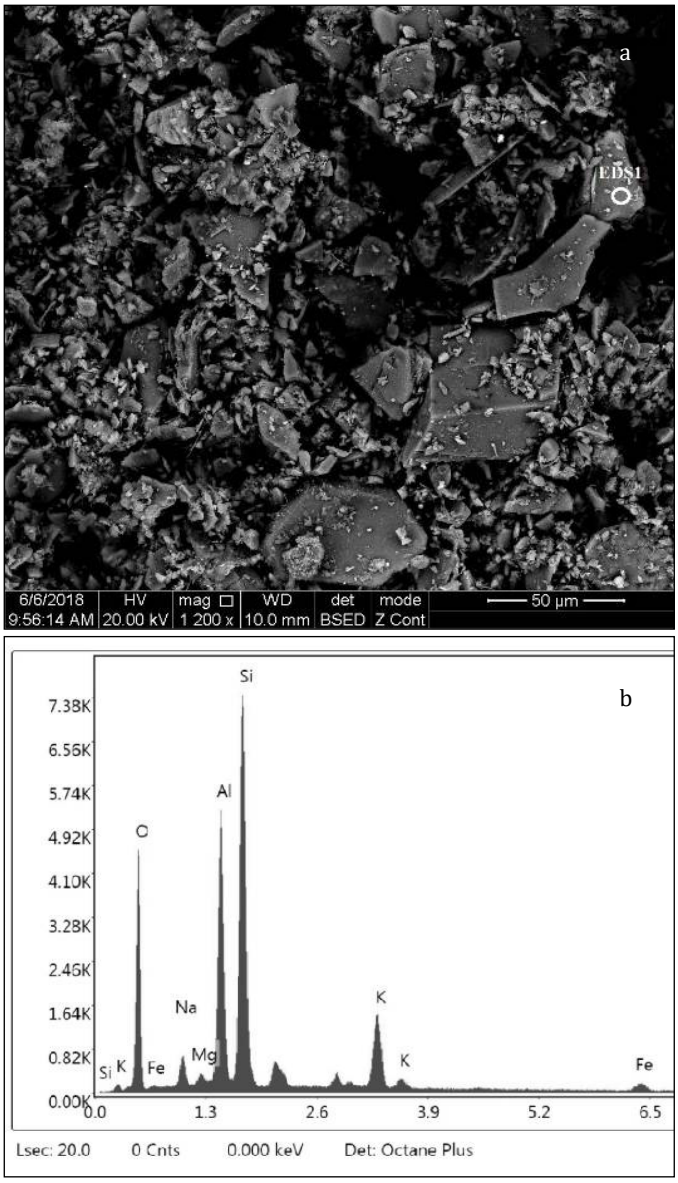


Figure 1. *(a) SEM-(b) EDS analysis example.*

1.2. Method

Mica flotation was originally selected to reduce the iron content and CCD method was chosen to plan flotation experiments and to analyze the results. However, according to initial results of mica flotation, the iron content was found to be insufficient. Therefore, a series of iron oxide flotations was needed to reduce the iron content to less than 0.1% in order to obtain superior grade feldspar. Therefore, the method used in this study can be called as two stage reverse flotation: mica flotation as stage I and iron-oxide flotation as stage II. Lab-scale Denver flotation machine was used for all flotation experiments. The test results were evaluated according to the iron content and weight yield of feldspar concentrates taken as sinking products by means of XRF analysis.

Before starting systematic studies, different collectors used in mica flotation in the literature were investigated with pre-trials for mica flotation and Procol CK 21 was found as the most effective collector among others. In stage I, Procol CK 21 which is an amine as a cationic collector and is produced by Ciba Specialty Chemicals was used as collector. The use of frother is not needed because of frothing property of chosen collector. The first conditioning was made in 55% solids ratio, the temperature was kept constant at 20^0C and the flotation time was 120 sec. In experiments; the effect of pulp density, pH, collector amount and air flow rate on the iron content and weight ratio of the concentrate (Recovery; %) were investigated. To determine the effect of each parameter, experiments were designed according to the Central Composite Design (CCD) which is one of the methods of response-surface methodology. These parameters were studied at 3 different levels and the α coefficient used to determine axial points in CCD was chosen as 2. In the software used, α value is suggested as 2 for 4 parameters. In various studies the α value is also suggested as 2 (Onay and Koca, 2019; Wang et al, 2016; Gungor et al, 2019) therefore the α coefficient was chosen as 2. The parameters and their levels are given in Table 2.

Table 2. *Selected parameters and their levels for Stage I.*

Parameters	Unit	Levels				
		-α	-1	0	1	+α
A (Pulp Density)	%	20	25	30	35	40
B (pH)		2.0	2.5	3.0	3.5	4.0
C (Collector Amount)	g/t	10	30	50	70	90
D (Air Flow Rate)	l/min	5.5	6.5	7.5	8.5	9.5

Number of experiments with α axial point at CCD was calculated as 29 by using following equation:

$$N = 2^k + 2\,k + n_c \quad (1)$$

Where N: number of experiments; k: number of factors, n_c: gives the number of midpoint experiments. After obtaining the test results, the results were subjected to variance analysis. Analysis of variance was performed according to 95% confidence interval. The equations proposed in the related module of the software used are based on the creation of reduced ANOVA tables and models. After the completion of the statistical analyzes, R^2 value indicating the compatibility of the obtained model equations with experimental data and PR^2 value indicating the prediction power of the model were examined. The optimum conditions optimizing iron content and the iron content and the yield of the concentrate taken under these optimum conditions were estimated. Experimental verification of the optimization study in the Stage I is also included. Design Expert software 10.01 was used for experimental design and the analysis of results.

Since Fe content remained at 0.14%, different collectors / collector mixtures recommended for iron-oxide flotation in the literature were also tested with preliminary studies. In the Stage II, iron oxide flotation was performed as reverse flotation to reduce iron content. 1:2:1 mixture of the A801+A825+A840 reagents which are petroleum sulphonates as an anionic collector produced by Cytec was selected as a collector. In the experiments, AF65 (produced by Clariant) was used as frother agent. At this stage, the amount of this collector mixture was studied and the initial conditioning was

performed at 55% pulp density. Pulp density, pH and airflow were kept constant at 30%, 3 and 8 l/min, respectively. The amount of collector was studied for 200-300-400 g/t as total amount.

2. Results and Discussion

As mentioned earlier, products from experimental studies were subjected to XRF analysis. Experimental studies were evaluated for the iron content and yield of feldspar concentrate taken as sinking product. The results are given separately for each stage.

2.1. Stage I

The values of the response variables calculated according to the results of chemical analysis of the products taken in the Stage I are given in Table 3. In this Table, solid rate (%), pH, the collector amount (g/t) and the air flow rate (l/min) are shown as A, B, C, D, respectively, and parameter levels are given as coded values.

Table 3. *The results of Stage I.*

No	A	B	C	D	Fe (%)	Rec. (%)	No	A	B	C	D	Fe (%)	Rec. (%)
1	-1	-1	-1	-1	0.20	93.46	16	+1	+1	+1	+1	0.13	84.61
2	+1	-1	-1	-1	0.20	94.78	17	-α	0	0	0	0.19	93.82
3	-1	+1	-1	-1	0.22	96.07	18	+α	0	0	0	0.16	89.21
4	+1	+1	-1	-1	0.21	94.65	19	0	-α	0	0	0.15	90.61
5	-1	-1	+1	-1	0.16	88.89	20	0	+α	0	0	0.18	89.02
6	+1	-1	+1	-1	0.15	90.04	21	0	0	-α	0	0.23	96.55
7	-1	+1	+1	-1	0.16	88.52	22	0	0	+α	0	0.12	81.68
8	+1	+1	+1	-1	0.15	86.88	23	0	0	0	-α	0.17	89.50
9	-1	-1	-1	+1	0.21	95.44	24	0	0	0	+α	0.16	88.28
10	+1	-1	-1	+1	0.20	93.3	25	0	0	0	0	0.19	94.89
11	-1	+1	-1	+1	0.22	96.59	26	0	0	0	0	0.17	90.12
12	+1	+1	-1	+1	0.20	94.11	27	0	0	0	0	0.17	91.44
13	-1	-1	+1	+1	0.15	89.17	28	0	0	0	0	0.16	91.26
14	+1	-1	+1	+1	0.13	86.10	29	0	0	0	0	0.17	88.81
15	-1	+1	+1	+1	0.15	85.86							

The results were subjected to the analysis of variance for both selected response variables. Subsequently, the reduced ANOVA charts and final models were generated by subtracting the terms that were statistically insignificant in the 95% confidence interval. In this study, the results are given as reduced ANOVA charts. R^2 and PR^2 values are also given. Besides, the results obtained are graphically interpreted for all parameters, and the graphs of interaction terms, if any, are presented in both two and three dimensions. In all graphs, parameters other than the parameter whose effect is examined are kept at medium level.

2.1.1. Iron content of the concentrate of Stage I

The results of iron content obtained in the experiments were subjected to variance analysis. In the related module of the software, linear model is proposed. However, when a Quadratic model was created and analyzed, it was determined that there was a low interaction between the collector amount (C) and the airflow (D). Then, an ANOVA chart was created by adding the CD interaction term to the linear model. Summarized ANOVA chart is given in Table 4.

Recommended model is statistically significant, with p value less than 0.05 (less than 0.0001); and the error term is also greater than 0.05 (0.8898). The R^2 and PR^2 values of the model are 0.9362 and 0.9044, respectively. Figure 2 (a) is a graph showing the relationship between the experimental results and the estimated results. As it can be seen from the figure, the predicted iron content values from the model represent approximately 94% of the experimental results. This shows the power of the model. The main effect graphs of the parameters examined in the process are given in Figure 2 (b) for all parameters. The model equations for coded values and actual values are given in Equation 2 and Equation 3, respectively.

$$Fe = 0.17 - 6.66*10^{-3}\,A + 4.16*10^{-3}\,B - 0.029\,C - 3.33*10^{-3}\,D - 3.75*10^{-3}\,CD \quad (2)$$

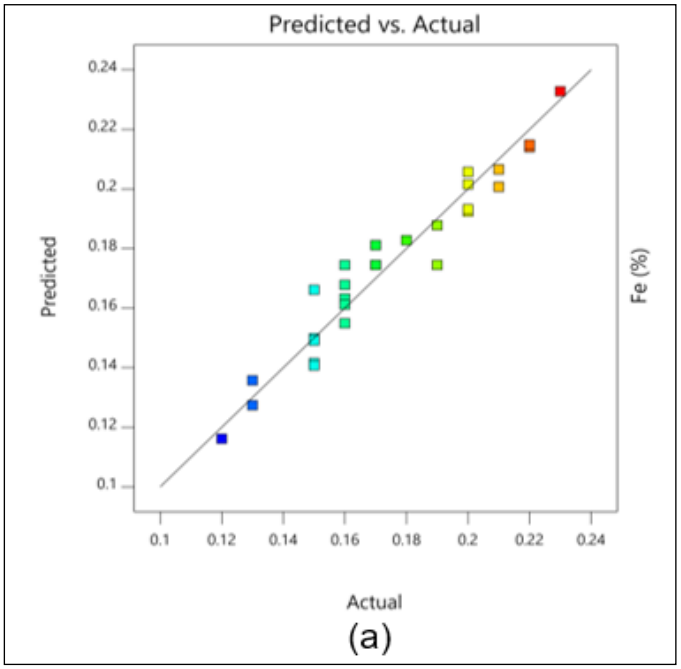
$$Fe = 0.22 - 1.33*10^{-3}\,A + 8.33*10^{-3}\,B - 5.21*10^{-5}\,C - 6.04*10^{-3}\,D - 1.88*10^{-4}\,CD \quad (3)$$

As it can be seen from the graph, the effect of A (Solid ratio), B (pH) and C (Collector amount) is significant at 95% confidence interval, while the effect of D (Air rate) is not statistically significant. When the P values in both the graph and ANOVA charts are examined, it is seen that the amount of collector is the most effective parameter. The graph shows that no parameter has a parabolic effect. In addition, when the ANOVA chart was examined, it was seen that the amount of collector interacted slightly with airflow (term CD). The interaction is graphically shown in Figure 3 in two dimensions (a) and in three dimensions (b).

As seen in Figure 3, the increase in the amount of collector causes a decrease in the iron content of the concentrate. However, this reduction occurs more slowly when the airflow decreases. This shows the interaction between these two parameters.

Table 4. *ANOVA chart and summary for the iron content of concentrate in Stage I.*

Source	P Values
Model	<0.0001
A	0.0005
B	0.0197
C	<0.0001
D	0.0569
CD	0.0784
Lack of fit	0.8898
R2	0.9362
PR2	0.9044



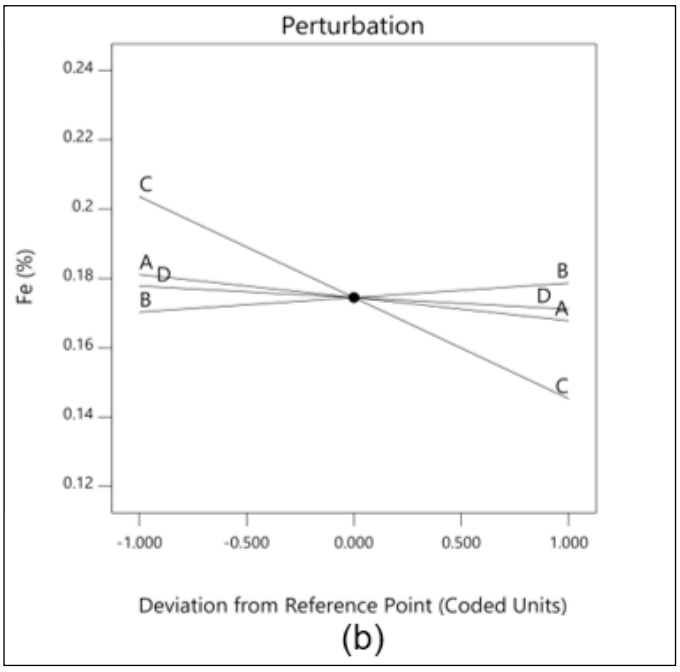


Figure 2. a) *Graph of experimental results versus predicted values for iron content of concentrate in Stage I;* ***b)*** *Main effect graphs of parameters on iron content of concentrate in Stage I.*

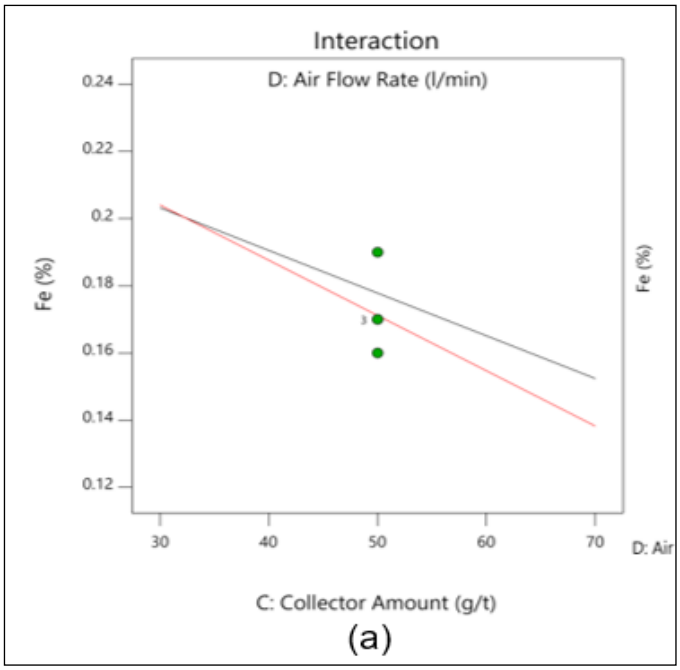


Figure 3. *Graph of the interaction between the collector amount and the airflow on the iron content of the concentrate in the Stage I; a) two-dimensional; b) three-dimensional*

2.1.2. The recovery of the concentrate of Stage I

The results of yield obtained in the experiments were also subjected to variance analysis. In the related module of the software, linear model is proposed. The ANOVA chart was created according to the linear model. Summarized ANOVA chart is given in Table 5.

Table 5. *ANOVA chart and summary for the yield of concentrate in Stage I.*

Source	P Values
Model	<0.0001
A	0.0304
B	0.3941
C	<0.0001
D	0.2077
Lack of fit	0.8983
R^2	0.8385
PR^2	0.7730

Recommended model is statistically significant with p value less than 0.05 (less than 0.0001); and the error term is also greater than 0.05 (0.8983). The R^2 and PR^2 values of the model are 0.8385 and 0.7730, respectively. Figure 4 (a) is a graph showing the relationship between the experimental results and the estimated results. As can be seen from the figure, the predicted yield values from the model represent approximately 84% of the experimental results. This shows the power of the model. The main effect graphs of the parameters examined in the process are given in Figure 4 (b) for all parameters.

The model equations for coded values and actual values are given in Equation 4 and Equation 5 respectively.

$$Recovery = 90.82 - 0.78\,A - 0.29\,B - 3.67\,C - 0.44\,D \quad (4)$$

$$Recovery = 109.74 - 0.16\,A - 0.59\,B - 0.18\,C - 0.44\,D \quad (5)$$

As it can be seen from the graph, the most effective parameter is the amount of collector (C). While the effect of solid ratio (A) was statistically significant at 95% confidence interval, the effect of pH (B) and airflow (D) parameters were not statistically significant. Similar to iron content analysis, no parabolic effect is observed in any parameter.

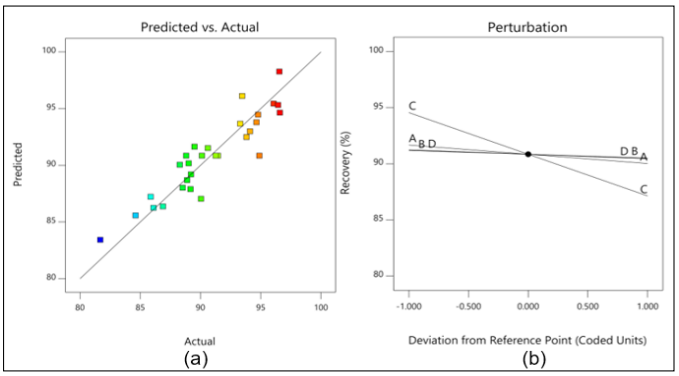


Figure4. *a) Graph of experimental results versus predicted values for yield of concentrate in Stage I, b) Main effect graphs of parameters on yield of concentrate in Stage I.*

2.1.3. The optimization of Stage I and verification results

With the help of the software, the estimation of the conditions that minimize the iron content of the sinking product (for coded values), the predicted values of the iron contents of the products taken under these conditions and the iron contents of the samples obtained from the experimental studies performed under the same conditions are given in Table 6.

The experimental data (0.14% Fe) corresponds to the estimated values in the 95% confidence interval (0.11% - 0.15% Fe). Therefore, it can be said that the obtained model is sufficient. In these conditions, the content of iron of floating product was found to be 0.97% Fe, and 88% of the feed was taken as feldspar concentrate. 51.42% of the iron in the feed was sunk. As a result, the values of all the response variables of the floating product and feldspar concentrate obtained from verification experiment in the optimum conditions matched up with the predicted value ranges calculated in the 95% confidence interval.

Table 6. *The results of verification tests of Stage I.*

Parameter	Value	Predicted value of Fe (%)			Experimental Value of Fe (%)
		Minimum	Average	Maximum	
A	+1	0.11	0.13	0.15	0.14
B	-1				
C	+1				
D	-1				

2.2. Stage II

In the Stage II, used sample was the sinking product of the first stage and with 0.14% Fe content. At this stage, the total amounts of collectors were determined as 200-300-400 g/t by preserving the 1:2:1 mixture ratio for A801+A825+A840. XRF results of these 3 experiments performed under these conditions are given in Table 7.

Table 7. *The effect of collector amount on iron content of feldspar concentrate in Stage II.*

Col. Amt. (g/t)	Recovery (%)	Iron Content (%)	Iron Dist. (%)
200	78.00	0.05	26.57
300	73.75	0.03	15.21
400	61.25	0.02	8.28

The increase in the amount of collector reduces the iron content of the concentrate, while the selectivity has also decreased. Therefore, the yield of feldspar taken as sinking product decreased rapidly. Considering that minus 0.1% Fe is the initial target, 200 g/t collector provides the target with 0.05 % Fe. As a result of this study, it can be stated that high quality feldspar which contains less than 0.1% Fe can be produced with the usage of a series collector, and the quality of feldspar can be increased significantly by increasing the amount of collector with a comprise on the feldspar yield.

On the other hand, the statistical design applied in the first stage and model equations of this stage were also acceptable according to the R2 and PR2 values of equations obtained. The model equation created especially for iron content is a model with a high predictive power with 0.9362 R^2 and 0.9044 PR^2 values. The result of the verification study carried out of this stage shows the power of model equations, too.

Conclusions

In this study, the possibility of reducing the iron ratio of feldspar taken from Aydın Soke region from 0.24% Fe to minus 0.1% Fe was investigated. The analysis shows that the ore consists mainly of plagioclase and alkaline feldspar and some quartz, and low amount of impurities such as muscovite, kaolin, iron containing chlorite and apatite minerals. In order to reduce the iron content, two stage reverse flotation was applied.

The mica flotation was applied in the stage I by using CCD methodology. XRF analysis was carried out on the products obtained from the experiments and the results were analyzed for the Fe content and the yield of concentrate.

The mathematical models of the process for these two response variables were examined. The correlation coefficient for the model of the iron content of the concentrate which is the first response variable was 93.62% and the PR^2 value of the model was 90.44%. These two values are over 90% and are very close to each other, and this situation shows that the model is very strong. According to the model and for the studied levels, the most effective parameter on the iron content was found to be the amount of collector. The models created for other response variable was also statistically significant. As a result, the iron content of feldspar was reduced from 0.24% to 0.14% by stage I.

In the stage II, the amount of the combination of A801+A825+A840 in the ratio of 1:2:1 determined as the most effective combination of collectors was studied. The used lowest amount of collector reduced the iron content in feldspar to 0.05% Fe, and this value coincided with the initial target as minus 0.1% Fe. This step was not optimized and it can be said that the iron content of the sinking product can be reduced to 0.02% Fe by increasing the amount of collector. However, increasing the amount of collector reduced the amount of sinking product by up to 60% by weight.

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Review

Analysis and recommendations on the use of polymer and phenol-based materials for coal mines

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A B S T R A C T

In this study, besides summarizing the properties of polymer materials used in underground coal mines, the problems that may arise in the use of polymer materials used in coal mines and the deficiencies of the relevant existing standards are discussed. Most of the safety accidents of polymer materials are encountered with results such as spontaneous combustion of materials, combustion of coal seams due to these combustions, and the release of toxic and harmful gases. The main causes of combustion accidents can be summarized as high reaction temperature, insufficient flame retardant, uncontrollable reaction process, defective standards and awareness of insufficient safety materials. Within the scope of this study, health problems that may be encountered due to the carcinogenic formaldehyde content of phenol-based filling materials will also be mentioned, and reasonable suggestions and measures will be discussed to prevent these and similar situations. The aim of this study is to establish a guide on the safe use of polymer materials in underground coal mines and correct understanding of the possible risk associated.

Keywords: *Polymer materials, Underground coal mines, Safety precautions, Spontaneous combustion, Reaction temperature, Flame tightness.*

Introduction

Polymer materials are widely used in coal mines and there are many types including polyurethane, epoxy resins, urea-formaldehyde resins for the main problems related to ventilation/leakage or cracks of coals (Liu 2021). In addition to that, some sodium silicate/polymer composite gels are recently being used for the prevention of coal spontaneous combustion (Ren et al. 2019). The polymers are mostly needed in terms of the isolation purposes and they are desired to show high strength, low reaction temperatures and no harm to human health. The scope of the application of phenol based filling materials in underground mining is summarized as in the following: consolidation of the structure of the weak coal strata to be produced or excavated, filling the cavity between steel support and ground, goaf stabilization, sealing of all entries connected to the fire area and isolating coal surface in the fire zone or area of spontaneous combustion. Accordingly, purposes of the usage of these abovementioned phenol based filling materials are provided as in the following:

i. Cavity filling

ii. Air-tight ventilation seals which will aid underground ventilation requirements

iii. Isolate the coal from air flow

iv. Fighting underground fires by constructing airtight barrier to cut off oxygen supply

The characteristics of the polymer materials have been summarized by Liu 2021 which are "high infiltration permeability, fast setting speed, short curing time, small shrinkage after grouting, good bonding and compressive properties, strong durability and impermeability". As well as the need for these polymers in mines increases day by day, the production statistics was reported as 40 000-50 000 tons/year by Liu 2021, for the coal mines (more than 2000 mines) in China. Keeping in mind the abovementioned statistics by Liu 2021, need for the polymers (specifically phenol based filling materials) in coal mines in Turkey is recently increased almost 30%-50% and the respective amounts for year 2019 and 2020 were reported as in Table 1 (Anon 2021).

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Table 1. *Usage of phenol based filling materials in Turkey in 2019 and in 2020 (Anon 2021).*

REGION	Total amount of usage in 2019 (tons)	Total amount of usage in 2020 (tons)
SOMA	1650	2880
ANKARA	300	400
ZONGULDAK	160	210
OTHERS	30	45
TOTAL	2140	3535

In addition, Çavuşoglu (2008) has a study which investigates the potential use of fly ash as a backfill material for the specific mine in Çayırhan-Turkey. Although the study abovementioned does not refer to the polymers or phenol based filling materials, the need for these materials in underground mine environments can be very well understood with this study. Zhang and Sun (2019) have carried out experiments and investigated mechanism of a polymer based material for reinforcing purposes of broken coal mass. In their study of Zhang and Sun (2019), authors have widely described the fractures, as primary and ongoing. They (Zhang and Sun 2019) have stated the fact that primary fractures result in expansion and transfix which initiates large number of initiated secondarily fractures, even as worse as coal rupture and many problems related to mechanical properties of coal mass (Shi et al. 2017, Wang and Yang 2017, Zhang and Sun 2019). Referring back to Zhang and Sun 2019 study, they have stated the fact that stress state changes for newly exposed coal seams and authors have expressed this as a reason of the damages of coal mass and rapid reduction of its bearing capacity. The importance of initial fractures and crack initiation is mainly because of the results abovementioned and the risks of inducing coal gas outburst disasters due to the result due to ineffective resist of the ground stress and gas expansibility (Zhang and Sun 2019).

Polymers, phenol based filling materials in specific has their significance based on the air leakage/ventilation problems which also has a vital role in underground mines. Phenol-based fillers are widely used in mining, and especially in underground coal mining, as an effective material for filling and blocking air leaks due to its heat resistance, flame retardancy, good sealing and ease of construction (Lei et al 2010, Wang et al. 2019). In addition to the usage in underground coal mining, Lei et al. (2010) have summarized their usage for civil construction, passenger and military aircrafts, marines and electronic applications. In Figure 1, a representative of phenol formaldehyde polymer condensation reaction is provided. The SEM microphotographs of the phenolic foam (Lei et al. 2010) is provided in Figure 2.

In addition, Ren et al. (2019) have investigated the novel sodium silicate/polymer composite gels and authors have suggested the usage of this polymer based material in order to prevent spontaneous combustion of coal. In their study of Ren et al. (2019), the authors have given information about the attempts of the researchers to prevent spontaneous combustion of coal by applying different technical measures and materials, up to year 2019. Ren et al. (2019) have cited the studies (Qin et al. 2015, Lu and Qin 2015) which includes pumping the top coal caving regions of coal drifts with foam cement, and some other papers (Hu and Wang 2013, Hu et al. 2014A, Hu et al. 2014B) which includes filling them with a polymeric material to seal air leakage. In the same context as in the Ren et al. (2019) study.

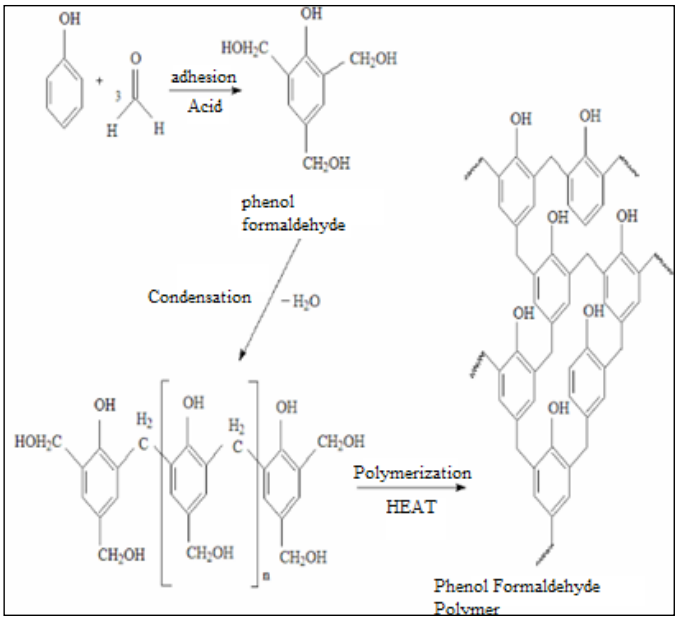

Figure 1. *Phenol formaldehyde condensation reaction (Frihart, 2005, Özlüsoylu 2016).*

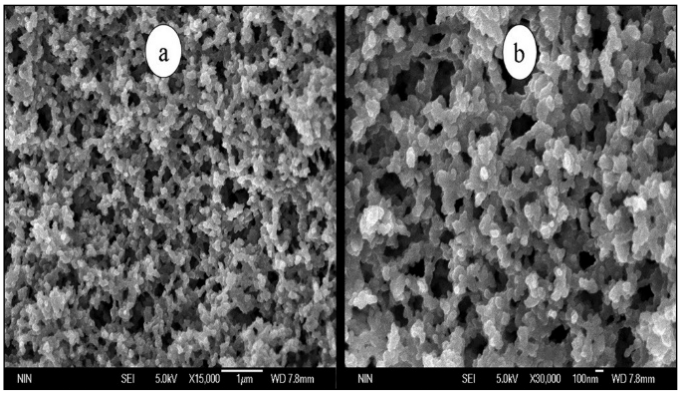

Figure 2. *The SEM microphotographs of the phenolic foam (adapted from the study of Lei et al. 2010)*

Fan et al. (2020) have proposed a novel plastogel which was claimed to have the ability to prevent and control fires in coal mines. The plastogel proposed by Fan et al. (2020) was described with its preparation by adding coagulant, polymer plasticizer and bentonite into the water glass solution. With the understanding of the abovementioned papers, it can be clearly emphasized the fact that polymer materials have been widely used in underground coal mining applications mainly for the purposes of sealing the air leakage and prevention of spontaneous combustion. In addition, these abovementioned polymer materials (with one, two or even three components (like plastogel by Fan et al. 2020)), should be tested in terms of their possible hazardous composition.

Güner and Öztürk (2019) have investigated deformability behavior of thin spray-on liners both experimentally and numerically. Although TSLs (thin spray-on liners) will not be detailed in this study, still they are polymeric or cement-based products that have been used for underground mine operations extensively for the purposes of rock support. Being produced based on the polymeric materials, TSLs should also be reconsidered and examined in terms of their hazardous content as regards to occupational health and safety.

Formaldehyde is one of these hazardous components of some of these polymer materials which are widely utilized in underground coal mines. In order to understand possible formaldehyde exposure, circumstances of exposure and results accordingly, report by AWES (2014) can be suggested to be a guide in the first place. As regards to USA-OSHA (Occupation Safety and Health Administration) standards formaldehyde concentration of gas produced by the reaction between resin and catalyst should be limited to 2 ppm.

In this study, polymers and phenol based filling materials were investigated in terms of the accidents caused by their utilization in underground coal mines. In addition, some examples of the accidents were provided in this context with their analysis. Not only the accidents based on the usage of these polymer materials and phenol based filling materials were examined but also some suggestions were provided by means of occupational health and safety.

1. Analysis and reasons behind the accidents resulting with polymer materials utilization in underground coal mines

Since chemical reaction is undergoing between the composites of the polymer & phenol based filling materials, each composite, final product and the chemical reaction should be taken into consideration all together in order to correctly address the hazardous structure of the specific material. To be clearer, -in the case the composites A and B forming polymer C, not only polymer formed (C) should be tested but also A and B along with the chemical reaction should be investigated in terms of their hazardous nature in specific atmosphere such as underground coal mining. Since underground coal mining is not directly in contact with the atmosphere, polymer materials (C), composites (A, B) and chemical reaction (between A and B) might be dangerous and hazardous in specific atmosphere of underground coal mining. Flash point temperature of each composite (A and B) should not be low, and it should be the first issue raised in underground coal mining application. The reason is rule of thumb, if the flash point temperature of the composites are lower than reaction temperature, that would result in fires that can trigger spontaneous combustion of coal. If the flash point is too high, then the polymer product is not classified as flame resistant. According to Liu (2021), polymeric materials and their composites along with the chemical reaction in between may cause carbonization failure, spontaneous combustion, explosion, fire, combustion, and toxic and harmful gases lead to poisoning and corrosion accidents. According to Küçük and Ilgaz (2015), accident causes by technical reasons (Güyagüler and Bozkurt 1993, Akkaya 2001, URL-1 2014, Durşen and Yasun 2012) were summarized as in the following:

1. Accidents caused by electricity and mechanization systems failures.

2. Explosions caused by dust, gas and radiation.

3. Explosives usages in mining operations.

4. Collapses and strata failures.

5. Haulage and water drainage system malfunctioning reasoned accidents and flooding.

6. Open pit fires, self-heating of coal related problems.

7. Sudden inrush, spontaneous combustion, pressurized gas discharges.

8. Accidents during the operations of coal preparation & mineral processing.

9. Low quality of mechanical maintenance, laboring and operational misguidances.

10. Accidents observed during the transportation, preparation, and usage of materials and instrumental tools.

11. Accidents due to mine environment constraints (heat, moisture, pressure, steam, noise, lighting, sliding surface, etc.).

12. Personnel and occupational health & safety related problems (ability, education, motivation, physical and mental state, personal attention, personal protection, etc.).

13. No proper working conditions and working environment (Küçük and Ilgaz 2015).

2. Examples of accidents and their causes

According to Liu 2021, a fire accident occurred in four mining areas (4238 fully mechanized working face in + 1030 m level) of a coal mine in Sichuan Province. This fire accident abovementioned occurred during the process of using organic polymer filling reinforcement material to deal with the top high caving area of the specified support, and it resulted in the closure of the whole mining area (Liu 2021). According to Liu 2021, direct causes of this abovementioned fire accident are: "rise in the internal temperature of the material due to heat release caused by the fire, ignition of wood stack, ignition of coal wall and return air side combustible and coal seam, fire". The indirect causes of the accident are stated as: "(i) Security technology management confusion. (ii) Mixing different polymer materials. (iii) Poor air circulation environment. Since the front is a closed falling space, which is almost not circulated, and the volume of the falling space is limited, a large amount of heat cannot be, forming a heat accumulation area. (iv) Spontaneous combustion of materials. Water injection cooling is not enough, the head of the water and water pressure is not large, can not inject a large number of cooling water at high temperature point, resulting in the combustion of polymer material itself, and then cause coal combustion" (Liu 2021). Not only accidents in terms of polymer based materials for the purposes of support and strata in mines but also gas inhaling and smoke based accident was observed in China, in specific mines (Liu 2021) observed. According to Liu (2021), toxic and harmful gases resulted in the death of a worker who was objected to the "yellow smoke" at the bottom of the drilling site door. Harmful gases were released by the chemical reaction of polymer materials filled in drilling site in a coal mine in Huaibei (5 # drilling site of 7118 working face). According to Liu (2021), direct causes of the accident is summarized as: "the filling material is not qualified, after filling the high temperature and toxic and harmful gas caused by poisoning death". Liu (2021) has also mentioned about the indirect causes of the abovementioned toxic and harmful gases' accident as: "(i) The procurement of filling materials is random. Not in accordance with the provisions of the company, from the normal channels of regular manufacturers import, acceptance. (ii) The material acceptance personnel in the ventilation area failed to work, only received quantity and did not check the quality. (iii) Poor hazard identification ability. Ventilation area gas inspectors in the third inspection smell, see yellow smoke but not informed. (iv) Unclear job responsibilities. Institution adjustment, the outburst prevention area has just been listed and has not been properly operated; The construction personnel directly used the filling material without identification, resulting in the chemical reaction of the filling material and producing high-level and toxic and harmful gases" (Liu 2021).

3. Problem in current standards and technical uncertainties

Usage of polymer materials in coal mines were issued by four standards which are being implemented since 2011 in China (Liu 2021). Existing situation about the application of these above-

mentioned standards is regarded as "not ideal" by Liu (2021) and yet it is also mentioned the fact that there are great objections to them in China (Liu 2021). By referring back and forth to Liu (2021), current standards in China were stated to only regulate the flame retardancy, antistatic ability and mechanical properties of polymer materials under normal temperature conditions. This abovementioned criticisms about the standards and their corresponding regulations are also valid for the ones which are being implemented in Turkey (See the example of a technical requirements of phenol based filling materials, Table 2)

Table 2. *Technical requirements of phenol based filling materials in Turkey.*

Technical Requirement	**Explanation**
Flame Retardancy	The foam will be flame resistant (Flame Retardant).
Reaction Temperature	The reaction temperature will be < 90°C.
Antistatic Property	The foam will be antistatic (≤109Ω).
Strength	Compressive strength shall not be less than min 0.02 MPa at 10% stacking.
Free Formaldehyde Content	The amount of free formaldehyde of the resin component used for foam formation will be less than 0.1% by weight.
Swelling Rate and Reaction Rate	High expansion rate and instant (immediate foaming) reaction.
Availability for Fire Fighting	It will be suitable for fire fighting activities.
Resistancy for Degradation in underground atmosphere	The foam formed as a result of the reaction is resistant to underground weather conditions, water, solution and biological disturbances.
Flash and Ignition Point	Low reaction temperature that will not self-ignite. The flammability of the reaction heat should be lower than the flash point temperature of the resin and catalyst used in the formation of the foam.
Blocker Property for Coal Spontaneous Combustion	It will stop the spontanous combustion of coal. It will stop the heating process of coal by isolating coal from air flow.
Long-term Availability of the Foam Structure	The stability of the foam structure will not change in the long term under underground conditions.
No Possible Effect on the Surroundings (sensors, etc) in Underground Atmosphere	No effect of foam application on the sensors in the underground atmosphere.
Property for Occupational Health and Safety Regulations	It should be proper for occupational health and safety regulation.

Liu (2021) have widely described the main problems in the standards (standards in China) of either for reinforcement and water plugging polymer materials (Table 3) and filling and sealing polymer materials (Table 4).

Table 3. *Main problems in the standards (standards in China) for reinforcement and water plugging polymer materials (Liu 2021).*

Problem in Standard	Problem Description
(1)	In AQ1089 - 2011, according to the different parts of reinforcement materials in coal and rock mass, it can be divided into C (coal reinforcement) and R (rock reinforcement). In the practical application process, it is difficult to distinguish in most cases.
(2)	The anti-aging performance index is expressed as 'no change in surface and no loss in mass', which is problematic. In the aging process, the volatilization of some solvent molecules will reduce their mass, but generally will not affect their mechanical properties.
(3)	The expression of " hazardous substance limit " in the standard is relatively vague. It should be concretized according to the material type, increase the flue gas toxicity test of the material, and quantitatively detect the content of toxic and harmful gases (HCN, NO, CO, halogen acid gas, etc.)

Table 4. *Main problems in the standards (standards in China) for filling and sealing polymer materials (Liu 2021).*

Problem in Standard	Problem Description
(1)	The materials in AQ1090 - 2011 were divided into N and P categories. In the actual grouting process, the materials used for hole sealing also need to bear pressure, so there is no need to classify them.
(2)	The standard flash point determination problem, generally A material can not measure the flash point, 50 ~ 60°C began to bubble, 80 ~ 90°C overflow pot, 100 ~ 110°C condensation; Material B is an acid without flash point. Substances with low boiling points (foaming agent) may be added in component A. After heating, the gas overflows and expands, and material A will bubble, overflow pot or even condense, which is difficult to measure.
(3)	The expansion ratio specified in the standard is not less than 25 times. Due to the different underground environments of coal mines, some need large expansion ratios, and some do not. In general, the higher the expansion ratio is, the lower the mechanical strength of the material is, and the expansion ratio of the material is not less than 10 times.
(4)	The expression of 'hazardous material limit' in the standard is vague and should be specified according to the type of material; The flue gas toxicity test of materials should be added to quantitatively detect the content of toxic and harmful gases (HCN, NO, CO, halogen acid gas, etc.).

The sector of polymer materials used in mining and underground coal mining is a rapidly developing sector and there are two problems that can be associated with the rapid development of this sector. First, the research and development potential of polymer reinforcement materials is insufficient. The second is that the users of polymer materials do not have enough information about the properties of the materials (Liu 2021). When the polymer materials usage standards in mining applications in Turkey (Table 2) and in China (Table 3, Table 4) are evaluated, it is understood that the users of polymer materials are not well-informed and research and development activities are not carried out at a sufficient level. For example, when the standards in Turkey (Table 2) are evaluated, it has not been determined in which standards these polymer materials should be tested for most of these technical requirements. Similarly, in the study of Liu (2021), author described the expressions in the standards for China (Table 3 and Table 4) as "problematic", "not clear enough", "indistinguishable", "cannot be generalized and should be specified specifically for the mine", "difficult to measure" and "do not need to be classified".

Conclusions

In addition to its high risk intense structure of underground coal mining, usage of polymer materials might have potential risks in terms of their hazardous and toxic content. Due to the high demand for the polymers with their available solutions to the problems in underground coal mining, corresponding industry is developing rapidly. This rapid development of polymer industry for mining applications results in two main problems: (i) lack of knowledge about the properties of polymers, (ii) lack of research and development about the applicability of these polymers. Based on the abovementioned problems for polymer materials, accidents or health disorders resulted by short-middle-long term objection might be unfortunately observed due to their hazardous and toxic structures. Considering the availability of polymer materials for the corresponding problems in underground coal mines, usage of polymer materials is inevitable. However, safe production of coal mines should be the top priority with the proper selection of polymer materials (least harmful, best convenient). Proper selection of polymer materials should include flue gas toxicity test and the content of toxic and harmful gases (HCN, NO, CO, halogen acid gas, etc.) should be quantitatively detected. In order to evaluate the abovementioned polymer material specifications (least harmful, best convenient), more research should be conducted in this field. With the help of the current developments and research carried out, technical requirements should be revisited and reworded. In this case, standards for the evaluation of polymer materials, the preference should be made according to test results obtained previously well-defined and described experimental conditions & standards. Technical uncertainties can only be overcome with the standard testing methods and technical specifications of the polymer materials should include the description of this standard testing methodology. Since, objection of the gases from these polymer materials (either during the chemical reaction or during the application) and interrelationship between this objection (short-middle-long term) and health issues is not yet well established, occupational health and safety precautions should be taken into consideration. Reviewing the occupational health and safety precautions, least harmful alternatives should be recommended by independent authorities. Cheaper alternative of polymers will always be available while their corresponding level of toxicity is questionable. Independent authorities should evaluate the polymer materials in terms of their potential risks (hazardous, toxic content) and price of each alternative should be out of their concern.

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Gine Cumhuriyeti Siguiri bölgesi altın cevherinin fiziksel ve kimyasal yöntemlerle zenginleştirilmesi

Enrichment of gold ore from the Siguiri basin of Republic of Guinea by physical and chemical methods

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Ö Z

Afrika sahip olduğu önemli maden kaynakları nedeniyle, tüm Dünya ülkelerinin ve yatırımcıların dikkatini çekmektedir. Kıta, özellikle yüksek altın tenörüne sahip büyük miktarda plaser altın yataklarına sahiptir. Bu çalışmada, Gine Cumhuriyeti sınırları içerisinde bulunan Siguiri havzasından alınan altın cevheri numunesinin zenginleştirilmesi gerçekleştirilerek alternatif proses akım şemaları oluşturulmuştur. Bu kapsamda, özgül ağırlık farkına göre zenginleştirme yapan Mozley masası ve Knelson ayırıcısı ile kimyasal zenginleştirme yöntemlerinden biri olan siyanür liçi deneyleri yapılarak cevher bileşimindeki altının kazanım olanakları ortaya koyulmuştur. Mozley masası ile üç kademe zenginleştirme sonucunda 186,91 g/t Au içeriğine sahip bir ağır ürün (konsantre) %89,1 kazanma verimi ile elde edilirken Knelson ayırıcısı ile üç kademe sonunda 149 g/t Au içeren bir konsantre %86,1 kazanma verimi ile elde edilmiştir. Gerçekleştirilen siyanür liçi deneyleri sonucunda ise 2 g/L NaCN derişiminde 48 saatlik liç ile %94,9 Au kazanma verimine ulaşılırken 1 g/L NaCN derişimi ve daha düşük liç süresi (24 saat) ile bu değer %91,9 olmaktadır.

Anahtar Sözcükler: *Plaser Cevher, Altın, Fiziksel Zenginleştirme, Siyanür Liçi, Santrifüj Ayırıcı*

A B S T R A C T

Since the Africa is endowed with important mineral reserves, it attracts the attention of all countries and investors. In particular, the continent has large deposits of placer gold ore with high gold content. In this study, the enrichment of gold ores samples collected from Siguiri basin within the borders of the Republic of Guinea was carried out and alternative process flowsheets were created. In this context, the recovery possibilities of gold in the ore were revealed using Mozley table and Knelson separator, which separate minerals according to the specific gravity difference, and cyanide leaching experiments, which is one of the chemical enrichment methods. As a result of three-stage enrichment with the Mozley table, a heavy product (concentrate) with 186.91 g/t Au grade was obtained with 89.1% recovery, while with the three-stage Knelson separator application, a concentrate assaying 149 g/t Au was obtained with 86.1% gold recovery. Furtermore, in the cyanide leaching experiment with 2 g/L NaCN concentration, 94.9% Au dissolution efficiency was achieved for 48 hours of leaching, yet this value was 91.9% with 1 g/L NaCN concentration and lower leaching time (24 hours).

Keywords : *Placer Ore, Gold, Physical Enrichment, Cyanide Leaching, Centrifugal Separator.*

Giriş

Batı Afrika kıyı ülkesi olan Gine Cumhuriyeti yaklaşık 13 milyon nüfusa sahip olup yüzölçümü 245857 km^2'dir. Başkenti Konakri olan ülkede ekonomi büyük ölçüde tarım ve madencilik faaliyetlerine dayanmaktadır. Sahip olduğu önemli altın rezervleri, birçok madencilik şirketinin dikkatini bu ülkeye çekmekte, altın rezervleri ağırlıklı olarak ülkenin kuzey doğusundaki Siguiri bölgesindeki Yukarı Nijer havzasında bulunmaktadır. Ülke yılda

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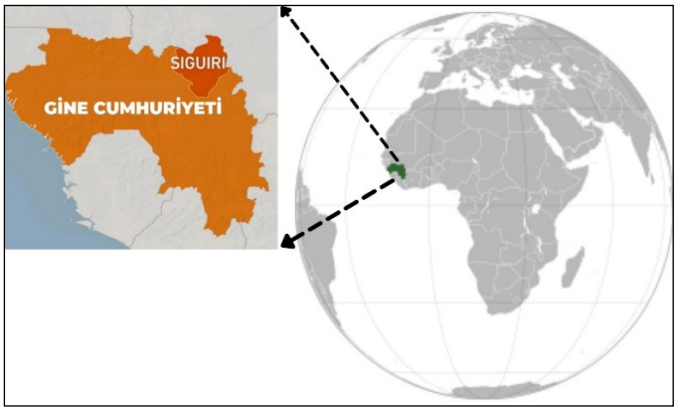
ortalama 8-10 ton altın üretmekte ve potansiyel rezervlerinin 700 ton olduğu tahmin edilmektedir (Punam vd., 2017; Signé, 2021). Birkaç şirket, Gine'de altın üretmek için endüstriyel olarak faaliyet göstermektedir (Vella, 2013; Veiga ve Gunson, 2020). Bunlar; AngloGold Ashanti'nin yan kuruluşu olan Guinea Gold Corporation, Dinguiraye Mining Corporation ve Avocet Madencilik'in bir yan kuruluşu olan Wega Madencilik'tir.

En önemli altın kaynağı olan Siguiri havzasında (Şekil 1) meydana gelen esasen iki tür altın yatağı mevcuttur. Bunlar, laterit veya kalsiyum fosfat mineralizasyonu ve yerinde kuvars damarıyla ilgili mineralizasyonlardır (Erwann vd., 2017). Gine'de altın madenciliği, geçmişten bugüne aile bireylerinin bir araya gelerek açtıkları yaklaşık 0,8-1 metre çapında ve 10-15 m derinliğindeki kuyulardan herhangi zorunlu bir havalandırma olmadan oldukça ilkel ve riskli koşullar altında yapılmaktadır (Veiga vd., 2006; Veiga ve Gunson, 2020). Kuyu derinlikleri bazı bölgelerde 30 metre derinliğe kadar inebilmektedir. Fakat, yeraltı su seviyesinin yüksek olması nedeniyle su seviyesinin altına el yordamı ile inememektedirler. Bu şekilde Gine'deki 200000 ila 300000 madenci tarafından üretilen altın miktarı senede 6 ton civarında olmaktadır ve bu üretim miktarı ülke için oldukça önemlidir (Amwele ve Groot, 2018). Ülkede uygulanan bu ilkel yöntemler sonucunda altın kazanma verimleri %5-%10 değerlerinin üzerine çıkamamaktadır. Riskli madencilik uygulamaları hem çalışanlar için önemli sağlık ve güvenlik sorunları doğururken, üretim sırasında oldukça önemli miktarda altın kayıpları oluşmaktadır. Gerek mevcut kaynakların daha verimli kullanılması gerekse de insan sağlığının korunması ve çevresel olumsuzlukların azaltılması amacıyla bu kaynakların sistematik bir şekilde değerlendirilmesi ve üretimde belli zenginleştirme süreçlerinin kullanılması oldukça önemli bir konudur (Hylander vd., 2007).



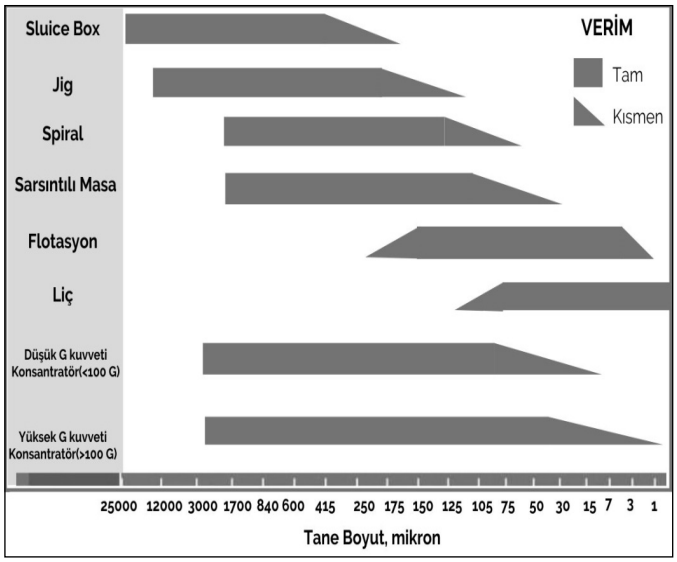
Şekil 1. *Gine Cumhuriyeti, Siguiri bölgesinin haritadaki yeri*

Bilindiği üzere, yerkabuğunda farklı şekillerde ve oluşumlar halinde bulunan altının üretiminde kullanılacak zenginleştirme süreçlerinin ve teknolojinin seçimi; cevherin türüne, oluşum şartlarına, cevher bileşimindeki diğer minerallerin fiziksel, kimyasal ve mineralojik özeliklerine, cevher içindeki altının boyutu ve içeriğine bağlı olmaktadır (Şen, 2007; Alp vd., 2008; Bayoğlu, 2013). Çizelge 1'de farklı cevherleşme türleri için uygulanabilecek zenginleştirme yöntemleri verilmektedir.

120 yılı aşkın süredir siyanür liçi dünya altın üretiminin %84'ünde kullanılmakta olup geri kalan %10'u gravite zenginleştirme, %4'ü flotasyon ve %2'si amalgamlaştırma ve diğer yöntemlerle ile gerçekleştirilmektedir (Deschênes, 2005; Celep vd., 2006; Bayoğlu, 2013; Gökelma vd., 2016). Plaser yataklarda serbest halde bulunan ve nabit altın içeren cevherlerden altının kazanılmasında özgül ağırlık farklılığına göre zenginleştirme işlemleri kullanılmaktadır (Folinsbee ve Hewitt, 1997; Meza vd., 1994). Bu yöntem, dünyanın en eski yöntemlerinden biri olup nabit altının sahip olduğu 19,3 değerindeki yüksek özgül ağırlığına dayanılarak yapılan bir zenginleştirme işlemidir (Sarıkaya, 2018). İnsanoğlu yaklaşık 6000 yıldan fazla bir süredir plaser altın madenciliği yaparak değerli metali ilk olarak bu tür yataklardan elde etmiştir. Bugüne kadar plaser yataklar, toplam dünya altın arzının üçte ikisinden fazlasını karşılamıştır. Zanaatkâr madenciler tarafından binlerce yıldan beri yapılan madencilik faaliyetinde kullanılan yöntem hep gravite esaslı olmuştur. Plaser altın yataklarında altın çoğunlukla granül, pul ve dal şeklinde (0,2-2 mm arası) serbest halde olabileceği gibi ana kayaç içerisinde bağlı olarak bulunabilmektedir. Özellikle serbest altın taneleri gravite ayırma yöntemleri ile direkt kazanılabileceği gibi bağlı taneler halinde bulunan altın ise gang adı verilen ana kayaçtan ayrılarak serbest hale getirilmek amacıyla bir öğütme işlemine tabii tutulmaktadır (Yüce vd., 2009). Bu tür cevherlerin bileşimindeki altın tanelerinin serbestleşme boyutuna bağlı olarak uygulanacak zenginleştirme yöntemi belirlenmektedir. Şekil 2'den görüldüğü üzere, zenginleştirme işlemlerinde daha iri boyutlarda jigler ve sluice kullanılırken daha küçük boyutlarda yarı merkezkaç kuvveti uygulanan spiral zenginleştiricilerin yanı sıra sarsıntılı masa, koni ve oluklar kullanılmaktadır. Bu boyutlarda elde edilen konsantrelerin temizlenerek daha yüksek Au içeriğine ulaşmak amacıyla Gemini masaları kullanılmaktadır. Ayrıca, daha küçük boyutlarda kullanılan Mozley masası ve gravite ile hidrodinamik kuvvetlerin yanı sıra merkezkaç kuvvetinden de yararlanılan Multi Gravite ayırıcısı (MGS), Knelson ve Falcon ayırıcıları kullanılmaktadır (Celep, 2005; Yüce vd., 2009; Yaşar, 2017; Özcan, 2019; Veiga ve Gunson, 2020).

Çizelge 1. *Altın kazanımında uygulanan yöntemler (Andrew, 1984)*

Yataklanma Tipi	Uygulanan Proses
Nabit Altın İçeren Serbest Halde Ufalanmış Damar Şeklindeki Cevher	Gravite ayırma + Amalgamasyon +Siyanür liçi
Nabit Altın İçeren Diğer Cevherler	Gravite ayırma + Amalgamasyon + Flotasyon + Siyanür liçi
Serbest Halde Ufalanmış Cevherler	Direkt siyanür liçi
Tellüridli Altın Cevherleri	Toplu flotasyon + Kimyasal oksidasyon + Siyanür liçi
Piritli Altın Cevherleri	Toplu flotasyon + Ergitme + Siyanür liçi
Bakırlı Kompleks Altın Cevherleri	Flotasyon + Siyanür liçi
Karbonatlı Altın Cevherleri	Kimyasal Oksidasyon + Siyanür liçi
Refrakter Altın Cevherleri	Kimyasal Oksidasyon veya mikronize öğütme + Siyanür liçi



Şekil 2. *Altının zenginleştirilmesinde kullanılan cihazlar (https://seprosystems.com/wp-content/uploads/2019/05/Gravity-Concentration.jpeg)*

Özellikle plaser altın cevherlerine ön zenginleştirme amaçlı bu tür fiziksel zenginleştirme yöntemlerinin uygulanması ile yüksek altın içeriğine sahip ön konsantreler elde edilebilmektedir. Elde edilen miktarca daha az olan ve yüksek Au içeriğine sahip bu ürünler normal koşullarda liç işlemine tabii tutulmayıp bunun yerine Acacia reaktör gibi özel altın kazanım sistemlerinde hızlı liç işlemine tabii tutulabilmektedir. Bu reaktörlerin kullanımı ile %98'in üzerinde toplam altın kazanımı değerlerine ulaşılabilmektedir (Celep vd., 2006).

Bu çalışma kapsamında kullanılan altın cevherinin temin edildiği, oldukça zengin maden kaynaklarına sahip Siguiri havzasının jeolojisi hakkında birçok çalışma (Steyn, 2012; Rutherford, 2021) olmasına rağmen bu cevherin zenginleştirilmesine yönelik yeterli teknik veri bulunmamaktadır. Gerçekleştirilen bu çalışma ile Siguiri havzasına ait altın cevherinin gravite ve siyanür liçi ile zenginleştirme olanakları araştırılmış ve alternatif proses akım şemaları oluşturulmuştur. Bu sayede hem bölge cevherlerinin hem de benzer plaser cevherlerin farklı yöntemlerle değerlendirilebilirliği ortaya koyulmuştur.

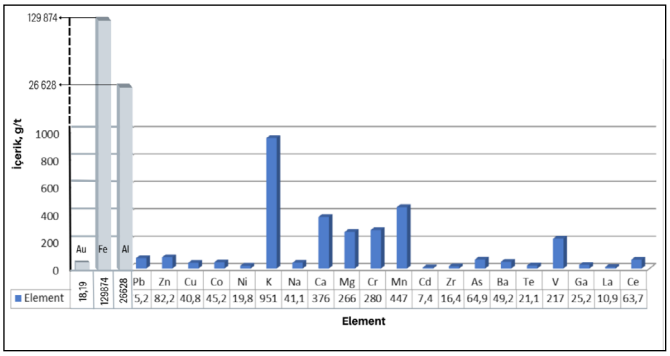
1. Malzeme ve yöntem

1.1. Deneysel çalışmalarda kullanılan numune

Deneysel çalışmalarda, Gine Cumhuriyeti'nin batısında bulunan dünyaca ünlü Siguiri havzası cevher numuneleri kullanılmıştır. Numuneler, Siguiri'ye bağlı Kouroussa şehrinin kuzey kısmında bulunan ve zengin altın yatakları ile tanınan bölgedeki altın cevheri alanından alınmıştır (Şekil 3). Geniş bir sahada yapılan çalışmalar kapsamında, 2-3 m derinliğinde ve belli aralıklarda açılan kuyulardan alınan numuneler toplanmış ve bu numuneler bir alanda stoklanmıştır. Büyük miktarda ve iri boyuttaki bu numunelerden temsili bir numune alma mümkün olmadığından, alınan cevherler mobil bir çeneli kırıcı ile boyutu küçültülerek numune azaltma işlemlerine tabii tutulmuştur. Cevher hazırlama numune azaltma kuralları dikkate alınarak azaltılan 100 kg'lık bir numune Türkiye'ye getirilmiştir.

Şekil 3. *Çalışmalarda kullanılacak numunelerin alınması amacıyla yapılan saha çalışması*

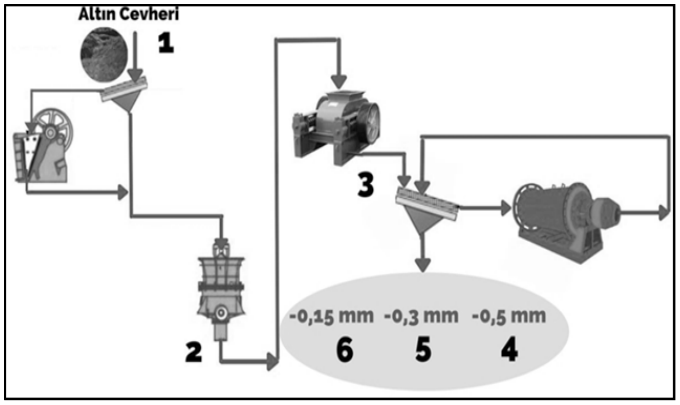
Gine Cumhuriyeti'nden alınan altın cevheri numunesi, ana kayaç türleri üzerinde tropikal ayrışma koşulları altında gelişen ancak bilinen ana kayaç altın yataklarının uzağında olan laterit ve saprolitler içerisinde homojen olmayan bir şekilde yayılmıştır. Yapılan mikroskobik çalışmalar ve kimyasal analizler sonucunda cevherin bileşiminde bulunan altın, demir oksitler ve kuvars ile kil mineralleri birlikte bulunmuştur (Veiga vd., 2006; Steyn, 2012; Siguiri Gold Mine, 2020). Şekil 4'te verilen kimyasal analiz sonuçlarına göre yüksek Fe içeriği (%12,99) demir oksitlerden, Al içeriği (%2,66) ise cevher bileşimindeki kil minerallerinden (Rutherford, 2021) kaynaklanmaktadır.



Şekil 4. *Altın cevherinin kimyasal analiz sonucu*

1.2. Yöntem

Bilindiği gibi altın üretim süreci; maden üretimi, cevher hazırlama ve zenginleştirme ile hidrometalurji gibi işlem adımlarından oluşmaktadır. Üretimi yapılan cevherin, öncelikle uygun bir tane boyutuna getirilmesi gerekmektedir. Bu işlemin amacı cevherin bileşimindeki altının serbest hale getirilmesi veya yüzey alanının arttırılmasıdır. Bu amaçla, numune hazırlama süreci sonrasında boyut küçültme deneyleri gerçekleştirilmiştir. Bu deneyler, Şekil 5'te verilen akım şemasına göre yapılmıştır. Akım şemasında belirtilen her noktadan (1, 2, 3, 4, 5 ve 6) alınan ürünlerin elek analizleri yapılmış ve her bir boyut küçültme işleminden sonraki boyut dağılımları belirlenmiştir.



Şekil 5. *Boyut küçültme işlemlerinin akım şeması*

Burada, elek analizi yapılacak noktalarda 1) tüvenan cevheri, 2) konik kırıcı ürününü, 3) merdaneli kırıcı ürününü, 4) -0,5 mm boyutuna öğütülmüş cevheri, 5) -0,3 mm boyutuna öğütülmüş cevheri ve 6) -0,150 mm boyutuna öğütülmüş cevheri ifade etmektedir.

Cevherin karakterizasyon çalışmaları ve boyut küçültme çalışmaları yapıldıktan sonra gravite etkisi ile zenginleştirme yapan Mozley masası ve Knelson ayırıcısı ile deneyler gerçekleştirilmiştir. En son aşamada ise cevherin siyanür liçi deneyleri gerçekleştirilmiştir. Tüm gravite ile zenginleştirme deneylerinde üç farklı boyutta hazırlanan numuneler (-0,5 mm; -0,3 mm ve -0,150 mm) kullanılmıştır. Çalışmalarda ilk olarak Mozley masası ile zenginleştirme işlemi yapılmıştır.

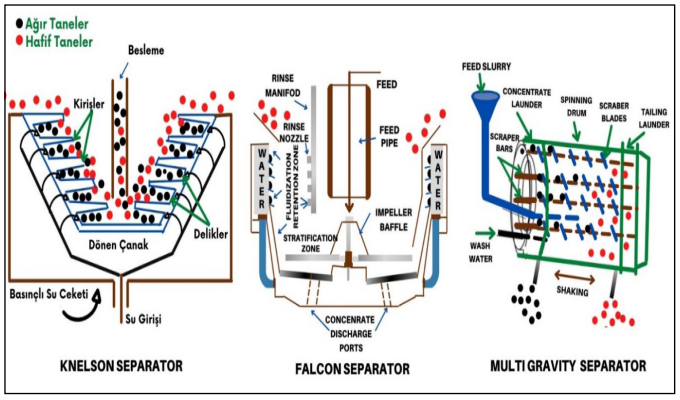
Bu deneylerde, düz yüzeyli Mozley masası kullanılmış (Şekil 6) ve ikinci aşamada ise santrifüj kuvveti ile çalışan Knelson ayırıcısıyla zenginleştirme deneyleri gerçekleştirilmiştir (Şekil 7).

Şekil 6. *Deneysel çalışmalarda kullanılan Mozley masası*

Fiziksel zenginleştirme işlemleri sonrasında, tüvenan cevherin siyanür liçi çalışmaları gerçekleştirilmiştir. Bu çalışmalar, 100 mikronun altında öğütülmüş orijinal numune ile gerçekleştirilmiştir. Bu kapsamda, öncelikle şişe döndürme (bottle roll) testi yapılmıştır. Bilindiği üzere bu test altının siyanür liçi ile kazanımında, altın çözünme verimi, asit tüketimi ve reaktif maliyetleri gibi hususlarda fikir vermektedir. Ayrıca, bu sonuçlar, pilot tesis ve ticari ölçekli liç devresinden elde edebilecek sonuçların doğru bir göstergesi olabilmektedir. Şişe döndürme testi, ince öğütülmüş cevherin, plastik bir şişe içerisinde %30-50 pülpte katı oranında ayarlanarak uygun bir çözücü ile çözündürülmesinden ibarettir. Altın için yapılan uygulamalarda genellikle pH 10,5 civarında tutulur. 1 g/L NaCN kullanılır ve işlem 24 saat devam ettirilir. Belirli zaman aralıklarında şişe durdurularak numune alınır. Alınan numunelerin altın içeriği analiz edilerek çözünme kinetiği tespit edilir (Dunne vd., 2019).

Gerçekleştirilen şişe döndürme testi sonrasında, cevher numunesi üzerinde laboratuvar ölçekli altın çözündürme (liç) deneyleri yapılmıştır. Bu deneyler, yine tamamı 100 mikronun altına indirilmiş numune ile 400 mL'lik beherlerde ve 400 d/dk karıştırma hızında gerçekleştirilmiştir. 100 g altın cevheri ve 233 mL su ilave edilerek istenen miktarlardaki liç reaktifleri (0,25; 0,5; 0,75; 1 ve 2 g/L NaCN) behere aktarılmıştır. Çözeltinin pH değeri kontrol edilmiş ve kireç ilavesi ile 10,5-11 arasına ayarlanmıştır. 24

saat liç süresi sonunda çözelti katı-sıvı ayırımı için filtre edilmiş, katı ve yüklü çözelti halinde iki ürün elde edilmiştir. Liç deneylerinden elde edilen yüklü çözeltideki Au analizleri indüktif olarak eşleştirilmiş plazma kütle spektrometresi (ICP-MS, Perkin ElmerELAN DRC-e 6000) cihazı ile gerçekleştirilmiştir. Bunun yanı sıra, fiziksel zenginleştirme işlemleri sonunda elde edilen katı ürünlerdeki altın içerikleri de altının çözeltiye alınması işleminden sonra yine aynı ICP-MS cihazı kullanılarak belirlenmiştir.

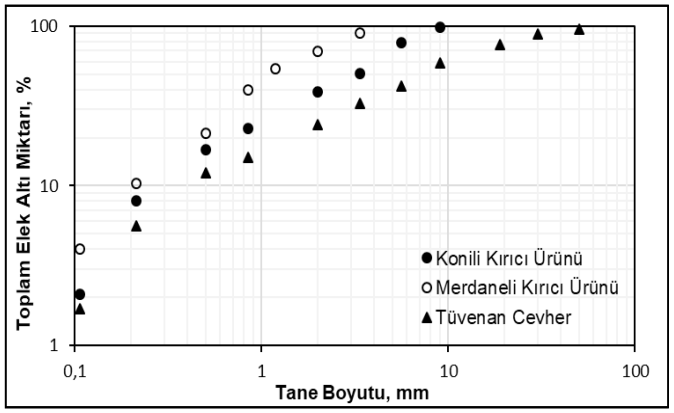


Şekil 7. *Deneysel çalışmalarda kullanılan Knelson ayırıcısı*

2. Deneysel çalışmaların sonuçları

2.1. Boyut küçültme deneylerinin sonuçları

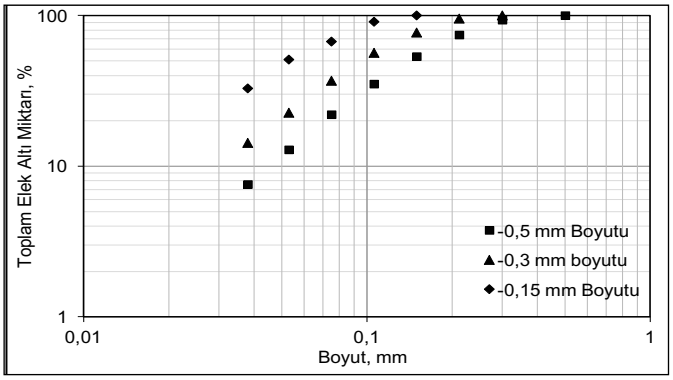
Kırma işlemleri sonrasında elde edilen ürünlerin boyut dağılımlarının belirlenmesi amacıyla kuru elek analizleri yapılırken, yaş öğütme sonrası elde edilen numunelerin elek analizleri yaş olarak yapılmıştır. Kuru olarak gerçekleştirilen boyut küçültme işlemlerinde sonra yapılan elek analizi sonuçları Şekil 8'de verilmektedir.



Şekil 8. *Kırma işlemleri sonrası ürünlerin elek analizi sonuçları*

Yapılan elek analizleri sonuçlarından, tüvenan cevherin (No:1) maksimum tane boyutunun 60 mm olduğu görülmektedir. Bu malzemenin %85'i 30 mm'nin altında olduğundan, kalan %15'lik +30 mm boyutlu kısmı çeneli kırıcıdan geçirilmiştir. Buradan elde edilen ürün ile orijinal cevherin -30 mm boyutu konik kırıcıya beslenen malzemeyi oluşturmuştur. Konik kırıcıda yapılan kırma işlemi sonrası elde edilen ürünün (No:2) maksimum tane boyutu 9 mm iken, d_{80} boyutu 6 mm olarak elde edilmiştir. Konik kırıcıdan elde edilen bu ürün son kademe kırma olarak merdaneli kırıcıya beslenmiş ve kırma işlemi sonrası 3,8 mm maksimum tane boyutuna sahip bir ürün (d_{80}:2,8 mm) elde edilmiştir.

Kuru olarak yapılan bu işlemler sonrasında elde edilen merdaneli kırıcı ürününü 3 farklı boyuta (-0,5 mm; 0,3 mm ve 0,150 mm) indirmek için bilyalı değirmen ile yaş öğütme yapılmıştır. Bilyalı değirmende pülpte katı oranı %60, bilya şarjı ise %45 olarak ayarlanmıştır. Malzemeyi 0,5 mm boyutu altına indirmek için 10+10 dakika, 0,3 mm boyutu altına indirmek için 15+20 dakika ve son olarak 0,150 mm altına indirmek için ise 20+25 dakika öğütme gerçekleştirilmiştir. Elde edilen ürünlere yapılan elek analizi sonuçları Şekil 9'da verilmektedir. Şekil 9'da, tamamı 0,5; 0,3 ve 0,150 mm boyutlarının altına öğütülen cevherin öğütme sonrası d_{80} boyutlarına bakıldığında; sırasıyla 0,28 mm; 0,19 mm ve 0,09 mm olduğu görülmektedir.



Şekil 9. *Öğütme işlemleri sonrası ürünlerin elek analizi sonuçları*

2.2. Gravite ile zenginleştirme deney sonuçları

Bu tür cevher yataklarında altının özgül ağırlığının yüksek olması nedeniyle, yerçekimi etkisi ile zenginleştirme işlemleri kullanılarak daha düşük özgül ağırlığına sahip diğer minerallerden ayırmak mümkündür. Mozley masası ve Knelson ayırıcısı bu çalışmada kullanılan gravite ayırıcılarıdır.

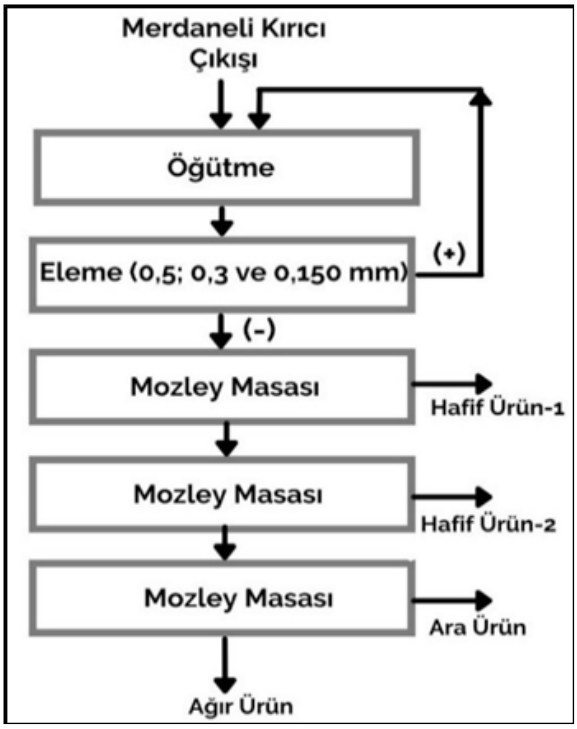
2.2.1. Mozley masası ile yapılan zenginleştirme deneylerinin sonuçları

Üç farklı boyuta hazırlanan numuneler (-0,5 mm; -0,3 mm ve -0,150 mm) ile yapılan Mozley masası zenginleştirme deneylerinde (Şekil 10), masanın eğimi 2°, yıkama suyu ise sırasıyla 2, 4 ve 6 L/dk olarak alınmıştır. Gerçekleştirilen zenginleştirme deneyleri sonrasında elde edilen ürünlerin altın analizleri yapılmış ve elde edilen sonuçlar Çizelge 2'de verilmiştir.

Çizelge 2'den görüldüğü üzere; üç farklı boyutta gerçekleştirilen zenginleştirme deneyleri sonucunda altın serbestleşme boyutunun 0,150 mm'nin altında olduğu görülmektedir. Bu boyutta yapılan gravite ayrımı ile toplam cevherin %76,3'ü, 0,49 g/t Au tenörü ve %1,9 altın kaybı ile hafif ürün olarak elde edilmektedir. Bunun yanı sıra, d_{100} boyutları daha iri olan (-0,5 mm ve -0,3 mm) boyutlarda elde edilen hafif ürünlerin yüksek Au içerikleri (-0,3 mm için 3,1 g/t; -0,5 mm için 7,6 g/t) altının bu boyutlarda bağlı taneler halinde bulunmasından kaynaklanmaktadır. Tamamı -0,150 mm boyutu altına öğütülmüş cevherin zenginleştirilmesi sonucu 186,91 g/t Au içeriğine sahip bir ağır ürün %89,1 altın kazanma verimi ile elde edilebilmektedir.

Çizelge 2. *Mozley masası ile üç farklı boyutta yapılan zenginleştirme deney sonuçları*

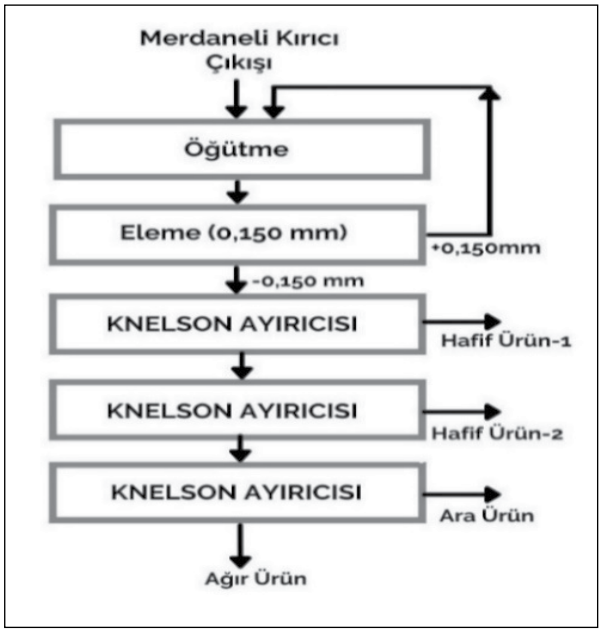
Boyut, mm	Ürünler	Miktar, %		Au İçeriği, g/t		Au Kazanma Verimi, %	
	Ağır Ürün	14,70		63,1		46,2	
	Ara Ürün	23,40		20,9		24,4	
-0,500 mm	Hafif Ürün-2	22,70		12,9		14,6	
	Hafif Ürün-1	39,20		7,6		14,8	
	BESLEME	100,00		20,07		100,0	
	Ağır Ürün	11,4		112,4		64,9	
	Ara Ürün	16,5		16,9		14,1	
-0,300 mm	Hafif Ürün-2	28,1		9,9		14,1	
	Hafif Ürün-1	44		3,1		6,9	
	BESLEME	100		19,74		100,0	
	Ağır Ürün	9,5		186,91		89,1	
	Ara Ürün	14,1		12,80		9,0	
-0,150 mm	Hafif Ürün-2	25,9	%76,3	0,78	0,49 g/t	1,0	%1,9
	Hafif Ürün-1	50,4		0,34		0,9	
	BESLEME	100,0		19,95		100,0	



Şekil 10. *Mozley masası ile farklı boyutlarda yapılan zenginleştirme deney akım şeması*

2.2.2. Knelson ayırıcısı ile yapılan zenginleştirme deneylerinin sonuçları

Knelson ayırıcısı ile gerçekleştirilen zenginleştirme deneyleri, tane serbestleşmesi nedeni ile daha iyi sonuçların alındığı -0,150 mm boyutunda yapılmıştır. Şekil 11'de verilen akım şemasına göre üç kademede gerçekleştirilen deneylerde, 1. ayırma kademesinde 1 L/d olan yıkama suyu, ikinci kademede 2 L/d ve son kademede ise 3 L/d olarak alınmıştır. Cihazın sabit G kuvveti değeri olan 60'da çalışılmıştır. Zenginleştirme deneyleri sonunda elde edilen ürünlere altın analizleri yapılarak sonuçları Çizelge 3'te verilmiştir.



Şekil 11. *Knelson ayırıcısı ile yapılan zenginleştirme deney akım şeması*

Çizelge 3. *Knelson ayırıcısı ile yapılan zenginleştirme deney sonuçları*

Ürünler	Miktar, %		Au İçeriği, g/t		Au Kazanma Verimi, %	
Ağır Ürün	11,3		149,00		86,1	
Araürün	7,0		24,65		8,8	
Hafif Ürün-2	37,1	%81,8	2,20	1,22 g/t	4,2	%5,2
Hafif Ürün-1	44,7		0,42		1,0	
BESLEME	100,0		19,57		100,0	

0,150 mm boyutu altındaki cevherin Knelson ayırıcısı ile yapılan zenginleştirme deney sonuçları incelendiğinde; cevherin %44,7 miktarı hafif bir ürün olarak 0,42 g/t Au tenörü ile elde

edilebilmektedir. Ayrıca, bu işlemde 149 g/t içeriğinde bir konsantre %86,1 verimle elde edilmiştir.

Elde edilen hafif ürünler birleştirildiğinde, %81,8 miktarında bir hafif ürün, 1,22 g/t Au içeriğine ve %5,22 Au kaybına sahip olmaktadır.

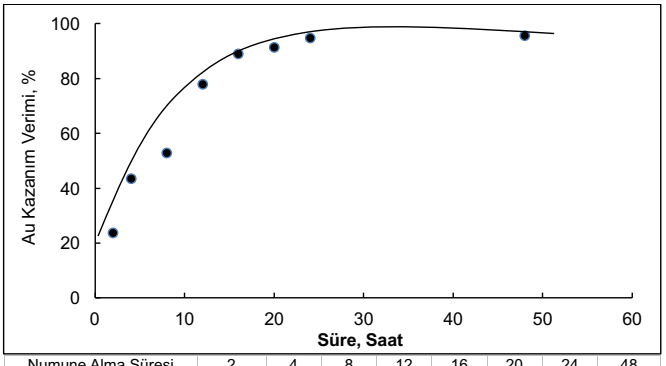
2.3. Kimyasal zenginleştirme (siyanür liçi)

Siyanür liçi, cevherlerden altın elde etmek için en yaygın kullanılan kimyasal yöntemlerden biridir. Altın kazanımı için siyanür liçinin kullanımı cevherin mineralojik yapısına (sülfürlü veya oksitli olmasına) ve cevherin diğer özelliklerine bağlıdır. Altın sülfürik, hidroklorik veya nitrik asitlerde çözünmez, ancak nitrik ve hidroklorik asitlerin bir karışımı (aqua regia) içinde ve seyreltik siyanür çözeltilerinde çözülebilir. Bu nedenle, siyanür hidrometalurjik proseste altın kazanımı amacıyla çözücü olarak kullanılmaktadır.

Bu çalışma kapsamındaki siyanür liçi çalışmaları, 100 mikronun altına öğütülmüş orijinal numune ile gerçekleştirilmiştir. Bu kapsamda öncelikle Çizelge 4'te verilen koşullarda şişe döndürme testi yapılmıştır.

Çizelge 4. *Şişe döndürme testi koşulları*

Tane boyutu	-106 mikron
Pülpte katı oranı	%30
pH	Kireç ilavesi ile 10,5-11 değerleri arasında tutulmuştur.
Şişeden numune alma süreleri	2, 4, 8, 12, 16, 20, 24, 48 saat

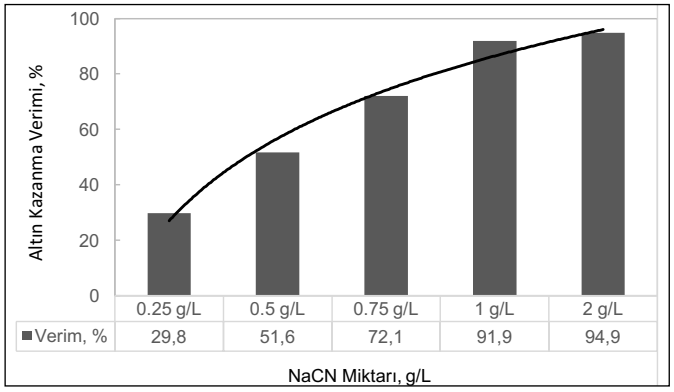


Numune Alma Süresi	2	4	8	12	16	20	24	48
Au Kazanım Verimi, %	23,7	43,5	52,9	77,9	88,9	91,4	94,8	95,6

Şekil 12. *Şişe döndürme test sonuçları*

Gine Cumhuriyeti altın cevherinin şişe döndürme testi sonuçlarına göre (Şekil 12); cevherin siyanürlenmesi ile altının %95,6'sının çözeltiye alınabileceği ortaya koyulmuştur. Süre 24 saat olduğunda altın kazanma verimi %94,8 olmaktır.

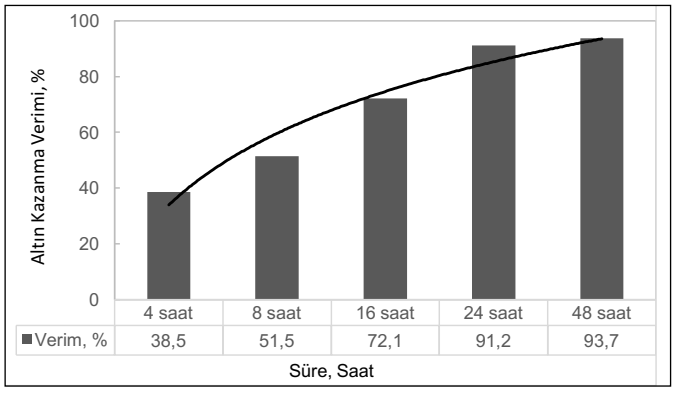
Altın cevherinin siyanür liçinde çözünme kinetiğinin ve mümkün olan en yüksek Au çözünme veriminin belirlendiği şişe döndürme testinin ardından laboratuvar ölçekli altın çözündürme (liç) deneyleri yapılmıştır. Liç deneyleri 400 mL'lik beherlerde ve 400 d/dk karıştırma hızında gerçekleştirilmiştir. Behere 100 g altın cevheri ve 233 mL su ilave edilerek, istenen miktarlarda liç reaktifleri (0,25; 0,5; 0,75; 1 ve 2 g/L NaCN) behere aktarılmıştır. Çözeltinin pH değeri kontrol edilmiş ve kireç ilavesi ile 10,5-11 arasına ayarlanmıştır. 24 saat liç süresi sonunda çözelti katı-sıvı ayırımı için filtre edilmiş, katı ve yüklü çözelti halinde iki ürün elde edilmiştir. Yüklü çözeltiden Au analizi ICP-MS yöntemi ile yapılmış olup katı ürün üç kez yıkanmış ve kurutularak altın analizi için hazırlanmıştır. 24 saat boyunca gerçekleştirilen ilk liç deneylerinde farklı NaCN derişimlerinde altın kazanma verimlerinin değişimi incelenmiş ve ulaşılan deney sonuçları Şekil 13'te verilmiştir.



	0.25 g/L	0.5 g/L	0.75 g/L	1 g/L	2 g/L
Verim, %	29,8	51,6	72,1	91,9	94,9

Şekil 13. *Siyanür derişiminin altın kazanımına etkisi*

Şekil 13'ten de görüldüğü gibi; 1 g/L'den düşük NaCN miktarlarında Au kazanma verimi yeterli seviyelerde olmayıp, 1 g/L NaCN ve 2 g/L NaCN miktarlarında bu değer sırasıyla %91,90 ve %94,90 olmaktadır. NaCN miktarı iki katına çıkarılmasına rağmen sadece %3'lük verim artışı nedeniyle 1 g/L NaCN derişimi dikkate alınarak farklı liç sürelerinde (4, 8, 16, 24, 48 saat) siyanür liçi deneyleri gerçekleştirilmiştir. Gerçekleştirilen bu deneylerin sonuçları ise Şekil 14'te verilmiştir.



	4 saat	8 saat	16 saat	24 saat	48 saat
Verim, %	38,5	51,5	72,1	91,2	93,7

Şekil 14. *Liç süresinin altın kazanımındaki etkisi (1 g/L NaCN)*

Farklı sürelerde gerçekleştirilen liç deneyleri sonuçlarından görüldüğü üzere; 24 saatlik liç işlemi sonucunda %90 çözünme verimlerinin üzerinde Au kazanma verimlerinin elde edilebildiği ve %2,5 verim artışı için toplam 48 saat liç süresine ihtiyaç duyulacağı belirlenmiştir. Bu yüzden 24 saatlik liç süresinin optimum çözündürme süresi olarak alınması uygun olacaktır.

Sonuçlar ve öneriler

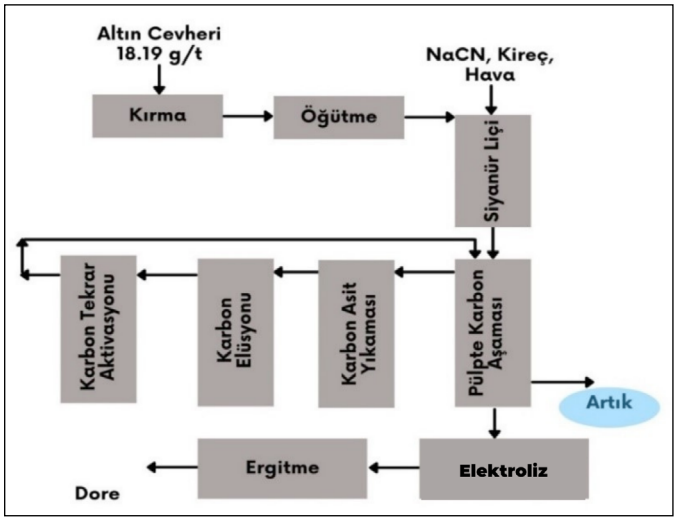
Demir oksitler, silikatlar ve kil mineralleri içeren Gine Cumhuriyeti altın cevheri 18,19 g/t Au içeriğine sahiptir. Farklı besleme boyutlarında yapılan gravite zenginleştirme deneyleri sonrasında 0,150 mm'nin altında yeterli tane serbestleşmesi olduğu belirlenmiştir. Mozley masası ile 0,150 mm boyutu altında yapılan zenginleştirme deneyi sonucunda toplam cevherin ~%76'sı Au içeriği 0,49 g/t ile hafif ürün (artık) olarak elde edilebilmektedir. Öte yandan 3. kademe sonunda 186,91 g/t Au içeriğine sahip bir ağır ürün (konsantre) %89,1 kazanma verimi ile elde edilebilmektedir.

Knelson ayırıcısı kullanılarak yapılan deneylerde benzer sonuçlar elde edilmesine rağmen, ürünün Mozley masası üze-

rinde daha kolay kontrol edilmesi nedeniyle Mozley masası daha iyi performans vermiştir. Buradaki zenginleştirme işlemi sonunda 0,42 g/t Au içeriğine sahip bir hafif ürün ile 149 g/t Au içeren bir konsantre %86,1 kazanma verimi ile elde edilebilmektedir.

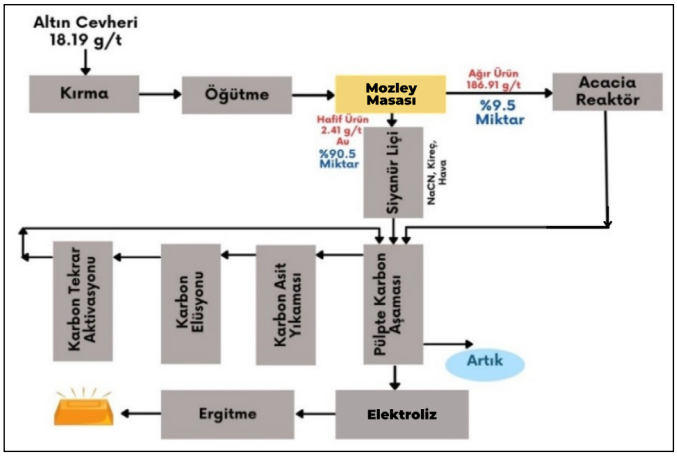
Bu çalışmalar sonucunda, cevherin doğası gereği siyanür liçi proseslerinde çok yüksek oranda altın kazanma verimleri elde edilmiştir. 2 g/L NaCN derişiminde, 48 saatlik liç ile %93,70 Au kazanma verimine ulaşılabilirken, daha düşük 1 g/L NaCN derişimi ve daha düşük liç süresi (24 saat) ile dahi altın kazanım verimi %91,2 olmaktadır. Bu çalışmada elde edilen sonuçlar ışığında, bu tür bir cevherin aşağıda açıklanan 3 alternatif proses ile değerlendirilebileceği sonucuna varılmıştır.

Alternatif-1: Siyanür liçi ile 18,19 g/t Au içeren cevherin doğrudan zenginleştirilmesi yapılabilir (Şekil 15).



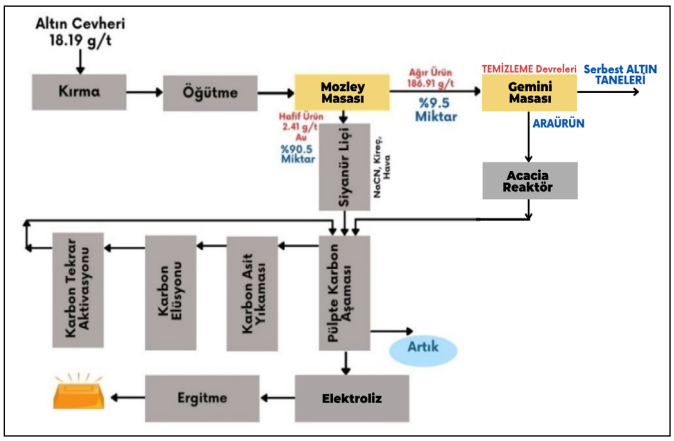
Şekil 15. *Alternatif-1 altın üretim proses akım şeması*

Alternatif-2: Ön zenginleştirme işleminde gravite ayırıcısı olarak kullanılan Mozley masasından elde edilen Au içeriği yüksek konsantre doğrudan Acacia reaktörüne gönderilirken, toplam beslenen cevherin %90,5'i olan 2,41 g/t ürün için siyanürleme işlemi yapılabilir (Şekil 16).



Şekil 16. *Alternatif-2 altın üretim proses akım şeması*

Alternatif-3: Ön zenginleştirme işleminde gravite ayırıcısı olarak kullanılan Mozley masasından elde edilen Au içeriği yüksek olan konsantreden, ayrıca Gemini masası kullanılarak birkaç kademe temizleme işlemi ile serbest altın kazanılabilir. Temizleme devresinde elde edilen ara ürün ise yüksek Au içeriği ile doğrudan Acacia reaktörüne gönderilirken, 1. gravite ayırıcısından elde edilen artık siyanürleme işlemine tabi tutulabilecektir (Şekil 17).



Şekil 17. *Alternatif-3 altın üretim proses akım şeması*

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Sülfürlü bakır-molibden konsantresinin asidofilik bakteriler ile seçimli biyoflotasyonu

Selective bioflotation of copper-molybdenum sulfide concentrate with acidophilic bacteria

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ÖZ

Bu çalışmada, sülfürlü bakır-molibden cevherinden (%0,458 Cu, %0,042 Mo) elde edilen toplu Cu-Mo konsantresinin (%12,02 Cu, %1,37 Mo) biyoflotasyon yöntemiyle zenginleştirme olanakları araştırılmıştır. Pülp pH'sı, bakteri türü ve bakteriyel kıvamlama süresi değişkenlerinin toplu Cu-Mo konsantresinden kalkopirit ve molibdenit konsantrelerinin kazanımı üzerine olan etkileri incelenmiştir. Toplu konsantredeki kalkopiritin bastırılması amacıyla asidofilik Acidithiobacillus ferrooxidans ve Acidithiobacillus thiooxidans türü bakteriler kullanılmıştır. Düşük pH'da (2-2,5) yapılan biyoflotasyon deneylerinde seçimliliğin olmadığı görülmüştür. Acidithiobacillus ferrooxidans ile pH 5-6 aralığında yapılan biyoflotasyon sonucunda, %3,2 Mo içeren %88,2 verimle bir molibdenit konsantresi ve %15,65 Cu içeren %80,6 verimle bir kalkopirit konsantresi üretilmiştir. Acidithiobacillus ferrooxidans türü bakterinin, Acidithiobacillus thiooxidans'a göre kalkopiriti daha etkin bir biçimde bastırdığı belirlenmiştir.

Anahtar Sözcükler: Asidofilik bakteriler, Bakır, Biyoflotasyon, Molibden

ABSTRACT

In this study, enrichment possibilities of bulk Cu-Mo concentrate (12.02% Cu, 1.37% Mo) obtained from copper-molybdenum sulfide ore (0.458% Cu, 0.042% Mo) by bioflotation method were investigated. The effects of pulp pH, bacteria type and bacterial conditioning time on the recovery of chalcopyrite and molybdenite concentrates from the bulk Cu-Mo concentrate were investigated. For the depression of chalcopyrite from the bulk concentrate, acidophilic Acidithiobacillus ferrooxidans and Acidithiobacillus thiooxidans bacteria were used. It was observed that there was no selectivity in bioflotation experiments at low pH (2-2.5). As a result of bioflotation with Acidithiobacillus ferrooxidans at pH 5-6, a molybdenite concentrate containing 3.2% Mo with 88.2% recovery and a chalcopyrite concentrate containing 15.65% Cu with 80.6% recovery were produced. It was determined that Acidithiobacillus ferrooxidans bacteria depressed chalcopyrite more effectively than Acidithiobacillus thiooxidans.

Keywords: Acidophilic bacteria, Copper, Bioflotation, Molybdenum.

Giriş

Molibden, yüksek sıcaklık dayanımı ve kararlılığı nedeniyle yüksek sıcaklık alaşımlarında, elektrikli ve elektronik cihazlarda, termal sprey kaplamalarda, tıbbi ekipmanlarda ve ayrıca havacılık ve savunma sanayinde yaygın olarak kullanılmaktadır (Yi vd., 2021). Çeliklere alaşım elementi olarak ilave edilen molibden, çeliklerin çekme dayanımını ve akma sınırını yükseltir, uzama ve kesit daralmasını azaltıcı etki yapar. Ayrıca, çeliklerin sertleşme kabiliyetini, tokluğunu, aşınma ve korozyon direncini arttırır (Polyak, 2012). Uluslararası Molibden Birliği'nin verilerine göre, molibden ürünlerinin %80'den fazlası metalurjide ve yaklaşık %13'ü kimya endüstrisinde kullanılmaktadır (UMB, 2022). Molibdenit (MoS_2), molibden cevherinin başlıca minerali olup dünyadaki molibden rezervlerinin neredeyse yarısı porfiri bakır yataklarındadır (Abdollahi vd., 2020; Bahrami vd., 2020). Bu tip yataklarda MoS_2 tenörü %0,01-%0,07 (veya daha yüksek) olduğunda, bakır konsantrelerinden yan ürün olarak molibdenitin kazanımı ekonomik olmaktadır (Yuan vd., 2019).

Sülfürlü bir bakır-molibden cevherinin zenginleştirmesinde, genellikle iki aşamalı flotasyon yöntemi uygulanır. İlk aşamada toplu flotasyon yapılarak kalkopirit-molibdenit mineralleri topluca kazanılır. İkinci aşamada seçimli flotasyon uygulanarak molibdenit ve kalkopirit konsantreleri ayrı ayrı elde edilir (Bulatovic vd., 1998; Bulatovic, 2007). Satılabilir molibdenit konsantresinin en az %40 Mo içermesi gerekmektedir (MTA, 2022). Kalkopirit konsantresinin ise %20 ve üzerinde Cu içermesi gerekmektedir

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(Even, 2009). Çoğu tesiste, kalkopirit, kalkozin gibi bakır sülfürler, sodyum hidrosülfür (NaHS), sodyum siyanür (NaCN), sodyum sülfür (Na_2S), Nokes (P_2S_5+NaOH) reaktifi vb. gibi bir bastırıcı kimyasal kullanılarak bastırılmakta ve molibdenit yüzdürülerek kazanılmaktadır (Park vd., 2020; Yi vd., 2021). Dünyada sülfürlü Cu-Mo cevherinin zenginleştirildiği tesislerden birisi, İran'ın güneydoğusunda Kerman şehrinde bulunan Sarcheshmeh Cu-Mo flotasyon tesisidir. Ortalama %0,7 Cu ve %0,025 Mo tenörlü cevherin beslendiği tesiste, yan ürün olarak molibdenit konsantresi üretilmekte ve iki ayrı aşamada kazanılmaktadır. İlk olarak Cu-Mo toplu konsantresi üretilmekte ve ikinci aşamada ise bakır-molibden konsantrelerinin birbirlerinden ayrılması sağlanmaktadır. Molibdenitin birinci ve ikinci aşamalarda kazanımı sırasıyla %65 ve %85-90'dır. Sülfürlü bakır ve demir minerallerinin bastırılması için yüksek miktarlarda (17,7 kg/t, toplam reaktif maliyetinin %58'i) Na_2S kullanılmıştır (Poorkani ve Banisi, 2005).

Bazı asidofilik bakteriler (örneğin; Acidithiobacillus ferrooxidans, Acidithiobacillus thiooxidans vb.), sülfürlü minerallerin biyoliçinde (örneğin; Cu sülfürler) ve refrakter altın cevherlerinin biyooksidasyonunda uzun yıllardır başarıyla kullanılmaktadır (Çiftçi, 2003, 2008; Çiftçi ve Akçıl, 2009). Daha önce yapılmış olan temel araştırma niteliğindeki çalışmalar, asidofilik bakterilerin biyoflotasyon ve/veya biyoflokülasyon amacıyla sülfürlü minerallerin zenginleştirilmesinde de kullanılabileceğini göstermiştir (Dwyer vd., 2012). Örneğin, asidofilik bakterilerden At. ferrooxidans'ın hücre yüzey yapısı, bu bakterinin bazı sülfürlü minerallere (pirit, kalkopirit vb. gibi) seçimli olarak adsorblanmasını sağlamaktadır. At. ferrooxidans, ferros demiri (Fe^{+2}) oksitleyebilir; bu nedenle, Fe^{+2} içeren mineralleri bir enerji kaynağı ve büyüme/gelişim substratı olarak kullanır. Böylece, bakteri hücrelerinin seçimli olarak bazı minerallerin yüzeyine adsorblanmasına/yapışmasına ve/veya yüzeyde bakteri-mineral etkileşimlerine bağlı olarak minerallerin hidrofilikliğinde (susever özelliğinde) artış meydana gelebilmektedir (Nagaoka vd., 1999).

Nagaoka vd. (1999) tarafından yapılan bir çalışmada, At. ferrooxidans türü bakteri kullanılarak saf haldeki beş sülfürlü mineralin (pirit, kalkozin, molibdenit, millerit ve galen) yüzdürülebilirlikleri araştırılmıştır. Kontrol (bakterisiz) deneylerinde, bu beş sülfürlü mineralin yüzdürülebilirlikleri %90-99 arasında değişmiştir. At. ferrooxidans kullanıldığında, pirit etkin şekilde bastırılmış ve %20'nin altında pirit kazanımı elde edilmiştir. Buna karşılık, At. ferrooxidans'ın diğer minerallerin flotasyonuna olumsuz etkisi daha az olmuştur. Diğer mineraller (kalkozin, molibdenit, millerit ve galen), %81-98 aralığında kazanılmıştır. Bu nedenle, At. ferrooxidans'ın piriti seçimli olarak bastırdığı sonucuna varılmıştır. Piritin bastırılmasının nedeni, diğer minerallere göre pirit minerali yüzeyine daha fazla sayıda bakterinin adsorblanmasından/yapışmasından dolayı olduğu belirtilmiştir. Pirit ve kalkopiritin flotasyonunda potasyum izopropil ksantat (PIPX) türü toplayıcı ilave edilmeden önce söz konusu mineraller At. ferrooxidans ile kıvamlandırıldığında, pirit önemli oranda (>%70) bastırılırken kalkopiritin büyük bir kısmı (>%80) yüzdürülerek alınmıştır. Bakterinin kalkopirit mineralini bastırma etkisinin pirite kıyasla daha az olduğu görülmüştür (Chandraprabha vd., 2005). Saf pirit ve kalkopirit minerallerinin Leptospirillum ferrooxidans bakterisi ile biyoflotasyonunda, kalkopirit mineralinin yüzeyinde daha fazla bakterinin adsorblandığı ve kalkopiritin pirite göre daha etkin bir şekilde bastırıldığı gözlenmiştir (Vilinska, 2007).

Sülfürlü minerallerin biyoflotasyonu konusunda günümüze kadar olan çalışmalar, genelde saf minerallerle ve mikro-flotasyon çapında yapılmıştır. Bu konuda mikroorganizmaların saf mineraller üzerindeki (FeS_2, FeS, $CuFeS_2$, PbS vb.) etkileri gözlemlenmiş olup cevher bazında yapılan çalışmalar oldukça sınırlıdır. Sülfürlü mineral(ler)i içeren cevherler ile yapılan sınırlı sayıdaki biyoflotasyon çalışmalarında, bu sürecin metalurjik performansına yönelik yeterli veri bulunmamaktadır. Ayrıca, literatürde sülfürlü Cu-Mo cevherinin/konsantresinin biyoflotasyonu üzerine herhangi bir çalışma da bulunmamaktadır. Sülfürlü minerallerin biyoflotasyonu konusunda daha önce yapılmış temel araştırma niteliğindeki (saf minerallerin kullanılması, mikro-flotasyon vb. gibi) çalışmalardan farklı olarak bu çalışmada, daha büyük ölçekte (hacimde) deneyler uygulanarak asidofilik bakterilerin konsantre üzerindeki etkileri araştırılmış ve biyoflotasyon sürecinin metalurjik performansına yönelik veriler elde edilmiştir. Bu kapsamda, At. ferrooxidans ve At. thiooxidans türü bakterilerin sülfürlü Cu-Mo konsantresinin seçimli flotasyonuna etkileri araştırılmıştır.

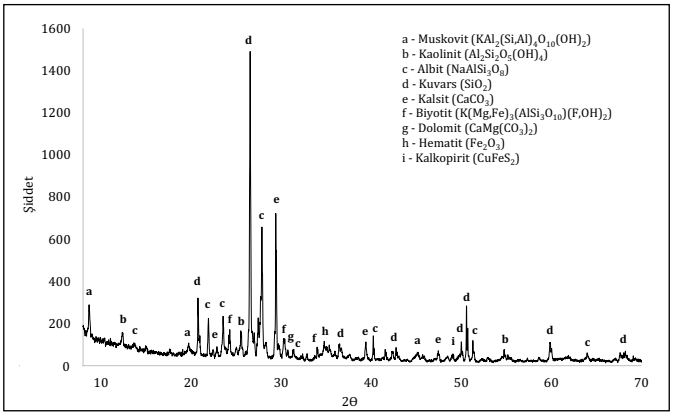
1. Malzeme ve yöntem

Tepeoba-Havran (Balıkesir) bölgesinden alınan sülfürlü bakır-molibden cevheri, %100'ü 1,7 mm'nin altında olacak şekilde çeneli kırıcıda kırılmış ve sonrasında çubuklu değirmende kontrollü bir şekilde %100'ü 106 µm'nin altına öğütülmüştür. Öğütülmüş cevherin d_{80} ve d_{50} boyutları, sırasıyla 0,05 mm ve 0,025 mm'dir. Kontrollü öğütme yapılmasına karşın, cevherde çok ince boyutlu (-0,02 mm) tanelerin miktarı oldukça yüksektir (~%46).

Cevher numunesinin kimyasal analizi Rigaku marka ZSX Primus 2 model X-ışınları Floresans Spektrometre (XRF) cihazı ve Perkin Elmer marka Optima 5300DV model İndüktif Olarak Eşleşmiş Plazma-Optik Emisyon Spektrometresi (ICP-OES) cihazı ile gerçekleştirilmiştir (Çizelge 1). Cevher numunesinin X-ışınları Kırınımı (XRD) analizi, Bruker marka D8 Advance Twin-Twin model XRD cihazı ile Cu K-α radyasyonunda (λ=0,154 nm) gerçekleştirilmiştir. XRD analizinde, cevher içinde sülfür minerali olarak sadece kalkopirit gözlenmiştir (Şekil 1). Ayrıca cevherin kuvars, muskovit, biyotit, kalsit, dolomit, albit, kaolinit ve hematit içerdiği belirlenmiştir.

Çizelge 1. *Bakır-molibden cevherinin kimyasal bileşimi*

Bileşen	%	Bileşen	%	Bileşen	%
SiO_2	55,74	CuO	0,56	NiO	0,01
Al_2O_3	18,64	MnO	0,12	Y_2O_3	0,01
CaO	5,60	P_2O_5	0,12	ZnO	0,01
K_2O	4,54	MoO_3	0,06	Mo	0,042
Fe_2O_3	2,95	Cr_2O_3	0,04	Cu	0,458
Na_2O	2,11	Rb_2O	0,03	Fe	2,06
MgO	1,77	SrO	0,03	S	0,608
SO_3	1,52	Cl	0,03	Kızdırma kaybı	5,38
TiO_2	0,65	ZrO_2	0,03		



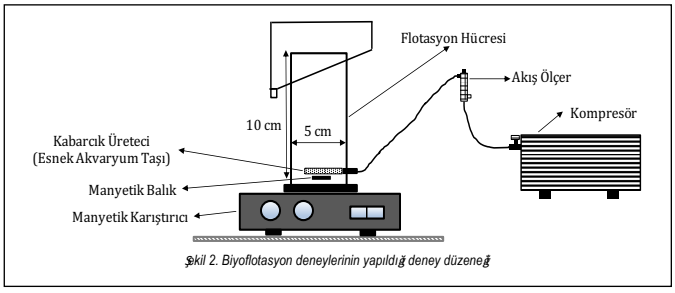
Şekil 1. *Bakır-molibden cevherinin XRD deseni*

Kimyasal analiz sonuçlarından, cevherin sülfürlü mineraller olarak %1,32 oranında kalkopirit ($CuFeS_2$), %0,07 oranında molibdenit (MoS_2) ve en fazla %0,22 oranında da pirit (FeS_2) mineralini içerebileceği hesaplanmıştır. Diğer taraftan, cevherdeki demirin büyük oranda oksitli/silikatlı mineraller olan hematit ile biyotitten kaynaklandığı XRD analiz sonuçlarından görülmektedir. Aynı cevher yatağı ile ilgili yapılan jeolojik/mineralojik bir çalışmada, cevherin oksitli demir minerallerini (hematit, manyetit, ilmenit vb.) içerdiği belirtilmiştir (Akay, 2013). Cevherin pirit mineralini neredeyse içermemesi ve demirin oksitli mineraller olarak bulunması nedeniyle biyoflotasyon deneylerinde demir analizleri yapılmamıştır.

Biyoflotasyon deneylerinde asidofilik bakterilerden Fe/S-oksitleyici Acidithiobacillus ferrooxidans ve S-oksitleyici Acidithiobacillus thiooxidans kullanılmıştır. Bakteriler, DSMZ (Almanya)'den saf kültür olarak temin edilmiştir. Bakteri kültürleri, 0,4 g/L $(NH_4)_2SO_4$, 0,4 g/L $MgSO_4 \cdot 7H_2O$, 0,2 g/L KH_2PO_4 ve 0,1 g/L KCl içeren besiyerinde geliştirilmişlerdir. Bakterilerin gelişiminde enerji kaynağı olarak At. ferrooxidans için ferros demir (Fe^{+2}) ve At. thiooxidans için elementel kükürt (S) besiyeri ortamına ilave edilmiştir.

Cevhere ilk olarak toplu flotasyon uygulanmış ve bu aşamada belirlenen optimum şartlarda yeterli sayıda toplu flotasyon deneyleri yapılarak üretilen toplu Cu-Mo konsantresi (%12,02 Cu, %1,37 Mo) üzerinde biyoflotasyon deneyleri gerçekleştirilmiştir. Toplu flotasyon uygulanmasının nedeni; cevherde yaklaşık %98 miktarında gang minerallerinin bulunması, kullanılacak kimyasal (bastırıcı, dağıtıcı vb. gibi) tüketimini artırmaktadır. Öğütülen cevherin de büyük bir kısmının (~%46) -20 µm boyunda olması nedeniyle şlam kaplama, mekanik taşıma vb. gibi flotasyon sürecini olumsuz yönde etkileyen durumlar söz konusu olabilmektedir. Bu nedenle, toplu flotasyonda bu tür gang minerallerinin sistemden uzaklaştırılması ile seçimli flotasyonda flotasyon verimi artırılmaktadır.

Kalkopirit ve molibdenitin etkin bir şekilde ayrılması için uygulanacak biyoflotasyon deneylerinde incelenen değişkenler ve değerleri Çizelge 2'de sunulmuştur. Biyoflotasyon çalışmalarında; pülp pH'sı, bakteri türü ve bakteriyel kıvamlama süresini içeren değişkenlerin seçimli şekilde molibdenit ve kalkopirit konsantrelerinin kazanımına etkisini belirlemek için deneyler gerçekleştirilmiştir. Bu aşamadaki deneysel çalışmalarda; toplu konsantre 130 d/dk'ya ve 30 °C sıcaklığa ayarlanmış çalkalamalı inkübatörde farklı pH ortamlarında (2 ve 5) bakteriler ile farklı sürelerde (0,5-168 saat) kıvamlandırıldıktan sonra konsantreye flotasyon işlemi uygulanmıştır. Deneylerde pH düzenleyici olarak H_2SO_4 ve NaOH, dağıtıcı olarak Na_2SiO_3, köpürtücü olarak MIBC kullanılmıştır (Çizelge 2). Biyoflotasyon deneyleri 150 mL hacimli hücrelerde yapılmıştır. Deney düzeneği Şekil 2'de gösterilmiştir. Bu deneylerde karıştırma işlemi için manyetik karıştırıcı kullanılmıştır.



Şekil 2. Biyoflotasyon deneylerinin yapıldığı deney düzeneği

Şekil 2. *Biyoflotasyon deneylerinin yapıldığı deney düzeneği*

Çizelge 2. *Biyoflotasyon deney koşulları*

Değişken	Değeri
Katı oranı	%10
pH düzenleyici	NaOH
pH aralığı (flotasyon için)	5-10
pH kıvamlama süresi	10 dk
Dağıtıcı cinsi	Na_2SiO_3
Dağıtıcı miktarı	1000 g/t
Dağıtıcı kıvamlama süresi	5 dk
Bakteri cinsi	At. ferrooxidans, At. thiooxidans
Bakteri sayısı	$1,2 \cdot 10^9$-$3,8 \cdot 10^9$ bakteri/mL
Bakteriyel kıvamlama süresi	0,5-168 saat
Köpürtücü cinsi	MIBC
Köpürtücü miktarı	100 g/t
Köpük alma süresi	1 dk
Karıştırma hızı	1000 d/dk
Hava akış hızı	2 L/dk

Her bir biyoflotasyon deneyinden elde edilen ürünler kurutulup tartılmış ve sonrasında kimyasal analizi yapılmıştır. Kurutulan ürünlerden temsili olarak alınan örnek numunelere çözündürme işlemi uygulandıktan sonra Mo ve Cu analizleri Perkin Elmer marka Optima 5300DV model ICP-OES cihazı ile gerçekleştirilmiştir.

2. Bulgular ve Tartışma

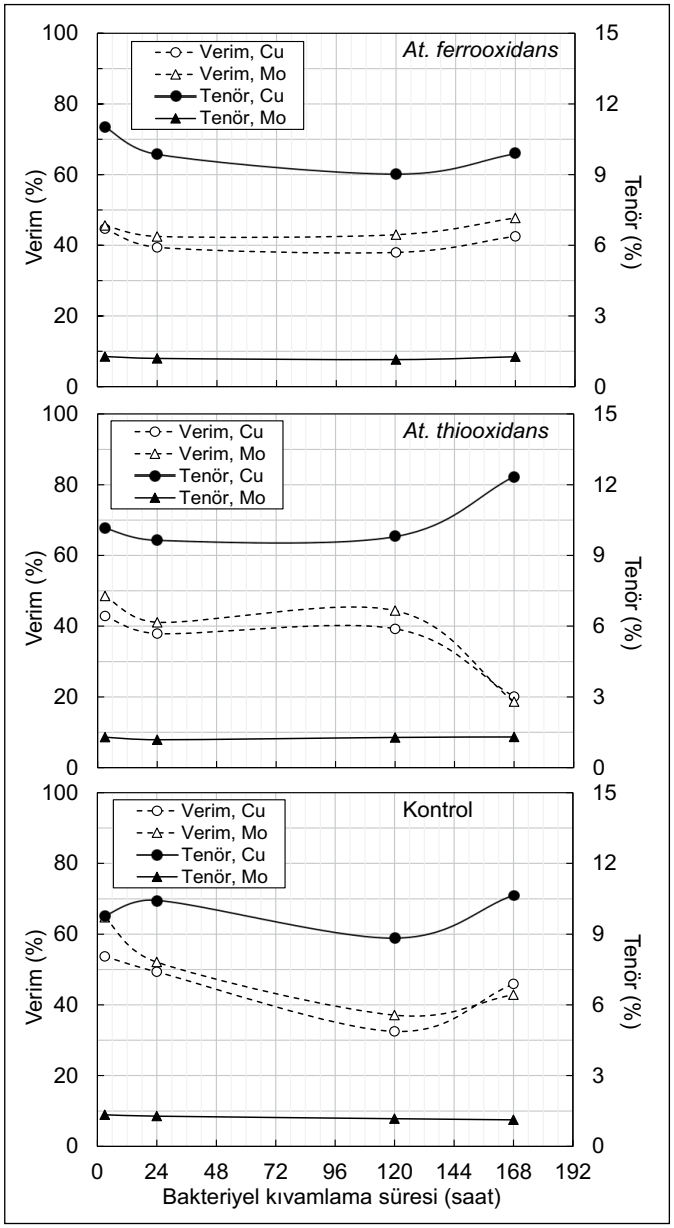
Asidofilik bakteriler optimum olarak pH 2-3 aralığında gelişmekte olup, pH 1-6 aralığında faaliyetlerini sürdürebilmektedirler (Silverman ve Lundgren, 1959; Kelly ve Harrison, 1989). Bu bakımdan, biyoflotasyon deneylerinde ilk olarak bakterilerin genel olarak en iyi gelişim gösterdiği pH 2-2,5 aralığında toplu konsantreye, bakteriler ile farklı sürelerde (3-168 saat) kıvamlama işlemleri tamamlandıktan sonra pH 10'da (pH düzenleyici olarak NaOH ile) flotasyon yapılmıştır. Kıvamlama işlemi, ilk olarak bakterilerin gelişimleri açısından ihtiyaç duyabileceği elementleri içeren besiyeri (0,4 g/L $(NH_4)_2SO_4$, 0,4 g/L $MgSO_4 \cdot 7H_2O$, 0,2 g/L KH_2PO_4, 0,1 g/L KCl) ortamında yapılmıştır. pH 2-2,5 arasında bakteriyel kıvamlama sonrası yapılan flotasyondan elde edilen sonuçlar Şekil 3 ve 4'te sunulmuştur.

Besiyeri ortamında pH 2-2,5 aralığında farklı sürelerde bakteriyel kıvamlama sonrası flotasyon deneylerinden elde edilen ürünlerde molibdenit mineralinin kalkopirit mineraline benzer dağılım göstermesinden seçimliliğin olmadığı görülmektedir (Şekil 3 ve 4). Bakteriler ile yapılan deneylerde molibdenit konsantresinde Cu veriminin %20,1-44,7 aralığında olmasının yanı sıra Mo veriminin de düşük olduğu (%18,7-48,5) belirlenmiştir. Aynı şartlarda yapılan bakteri içermeyen kontrol deneylerinde ise molibdenit konsantresinde Mo verimi %37,1-64,8 ve Cu verimi %32,5-53,7 arasında değişmektedir.

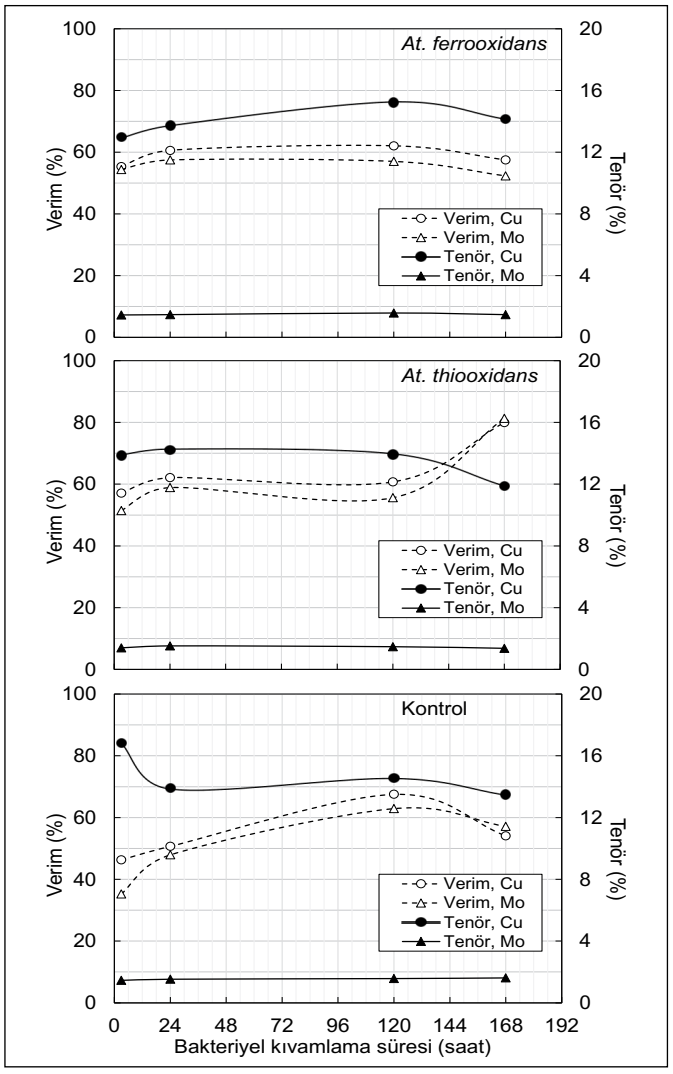
At. thiooxidans ile yapılan biyoflotasyon deneylerinde 168 saat kıvamlama süresinde kalkopirit konsantresinde Cu veriminin %79,9 gibi yüksek değere ulaşmasına karşın, Mo veriminin de oldukça yüksek (%81,3) olması, kalkopiritle birlikte molibdenitin de etkin bir şekilde bastırıldığını ve seçimliliğin olmadığını göstermektedir (Şekil 4). Kontrol (bakterisiz) deneylerinde kıvamlama süresi artışıyla molibdenit konsantresinde hem Mo hem de Cu verimlerinde belirgin bir azalma meydana gelmiştir (Şekil 3). Örneğin, kontrol deneylerinde kıvamlama süresi 3 saatten 120 saate yükseltildiğinde molibdenit konsantresinde Mo verimi %64,8'den %37,1'e azalmıştır. Bu nedenle, molibdenit mineralinin hidrofobikliğindeki azalmanın bakterilerin etkisiyle olmadığı, besiyerinde kullanılan kimyasalların ve/veya asidik ortamda

çözünmüş iyonların etkisiyle olabileceği değerlendirilmiştir. Besiyeri bileşenleri kullanılmadan yapılan biyoflotasyon deneylerinden elde edilen sonuçlar, besiyeri ortamındakine benzer şekilde kalkopirit ve molibdenit flotasyonun düşük seçimlilikle gerçekleştiğini göstermiştir.

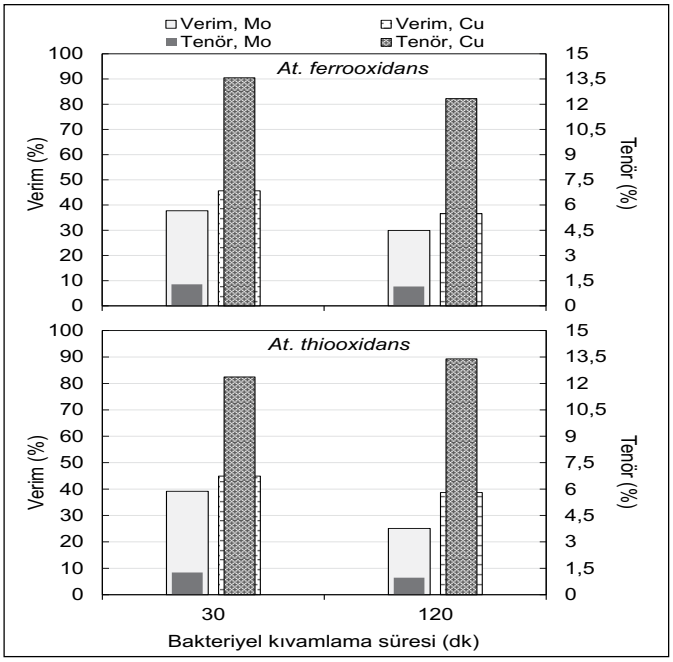
Biyoflotasyon deneylerinde 3 saat ve daha uzun süre uygulanan bakteriyel kıvamlama sürelerinin seçimliliğe olumlu yönde belirgin etkisi olmadığından daha az kıvamlama sürelerinde (30 dk ve 120 dk) biyoflotasyon deneyleri uygulanmıştır (Şekil 5 ve 6). Literatürde, bakteriyel kıvamlama süresi olarak 2 dk (Nagaoka vd., 1999), 15 dk (Hosseini vd., 2005) gibi çok daha az sürelerin uygulandığı biyoflotasyon çalışmaları da bulunmaktadır. At. ferrooxidans'ın pirit mineraline diğer sülfürlü minerallerden daha hızlı adsorblandığı ve pirit yüzeyine adsorblanmasının 10-15 dk arasında denge durumuna ulaştığı belirtilmiştir (Das vd., 1999; Sharma vd., 1999; Natarajan ve Das, 2003; Chandraprabha vd., 2004a). Ayrıca, At. ferrooxidans'ın kalkopirit ve arsenopirit minerallerine göre pirite daha fazla sayıda adsorblandığı bildirilmiştir (Chandraprabha vd., 2004a,b; Chandraprabha vd., 2005).



Şekil 3. *Bakteriler ile kıvamlama (pH 2-2,5) sonrası yapılan flotasyonda molibdenit konsantresinin tenör-verim değişimi*



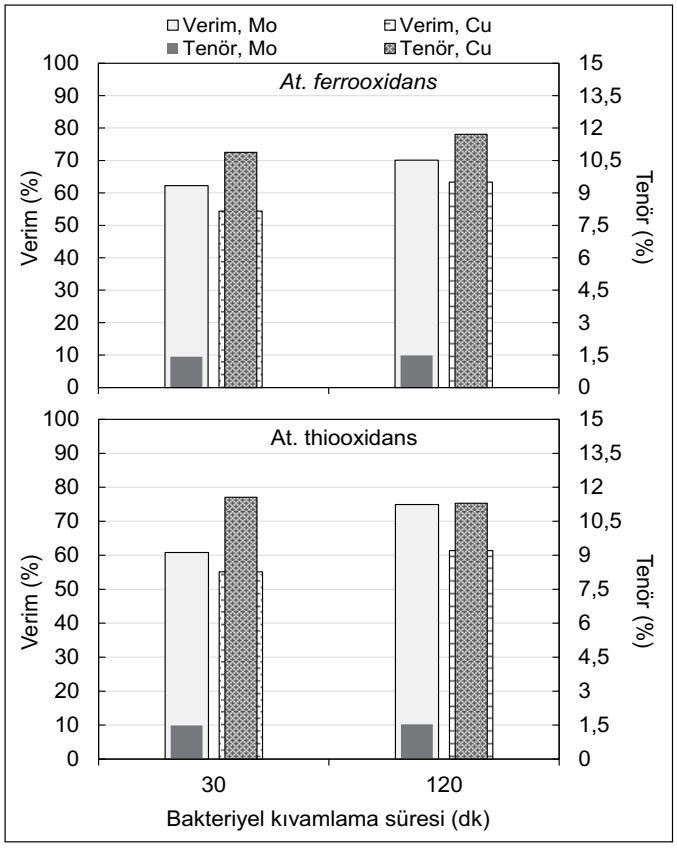
Şekil 4. *Bakteriler ile kıvamlama (pH 2-2,5) sonrası yapılan flotasyonda kalkopirit konsantresinin tenör-verim değişimi*



Şekil 5. *30 dk ve 120 dk bakteriyel kıvamlama (pH 2-2,5) sürelerini içeren biyoflotasyonda molibdenit konsantresinin tenör-verim değişimi*

Şekil 5 ve 6'dan görülebileceği gibi, kıvamlama süresinin 30 dakikadan 120 dakikaya artırılmasının kalkopiritin bastırılmasını olumlu yönde etkilediği, bu süre artışıyla ayrıca molibdenitin hidrofobikliğinde de azalmanın olduğu belirlenmiştir. Ancak, 3 saat ve daha fazla sürenin uygulandığı bakteriyel kıvamlama deneylerinde ise molibdenitin hidrofobikliğinin daha yüksek olduğu, molibdenit konsantresindeki Mo verimlerinden de görülmektedir (Şekil 3 ve 4).

Bu kapsamda, benzer şartlarda klasik seçimli flotasyon deneyleri gerçekleştirilmiştir. Toplu konsantreye pH 2-2,5 aralığında 10 dk kıvamlama işlemi uygulandıktan sonra bastırıcı olarak $Na_2O_5S_2$ ve NaCN kullanılarak pH 10'da yapılan seçimli flotasyon deneylerinde de molibdenitin hidrofobikliğinin önemli oranda azaldığı belirlenmiştir. Örneğin, aynı bastırıcılar kullanılarak pH 10'da kıvamlamanın yapıldığı deneylerde molibdenit konsantresindeki Mo verimi %80'lerin üzerinde elde edilirken, pH 2-2,5 aralığında ise Mo verimi yaklaşık %35'lere düşmüştür (Çizelge 2).



Şekil 6. *30 dk ve 120 dk bakteriyel kıvamlama (pH 2-2,5) sürelerini içeren biyoflotasyonda kalkopirit konsantresinin tenör-verim değişimi*

Çizelge 3. *pH 2-2,5 aralığında kıvamlama sonrası pH 10'da farklı bastırıcılar ile yapılan seçimli flotasyon sonuçları*

Bastırıcı cinsi	Ürünler	Ağırlık (%)	Tenör (%)		Verim (%)	
			Cu	Mo	Cu	Mo
$Na_2O_5S_2$	Konsantre	17,16	19,58	2,98	27,9	37,3
	Artık	82,84	10,47	1,04	72,1	62,7
	Besleme	100	12,04	1,37	100	100
NaCN	Konsantre	14,76	14,62	3,18	18,0	34,8
	Artık	85,24	11,56	1,03	82,0	65,2
	Besleme	100	12,02	1,35	100	100

Literatürde, pülp ortamında bulunması muhtemel Ca^{+2}, Mg^{+2}, Na^+, Cu^{+2} vb. gibi çeşitli katyonların molibdenit kazanımında önemli bir etkisi olduğu belirtilmiştir (Jeldres vd., 2016; Castro, 2018; Lin vd., 2020). Özellikle Ca^{+2} ve Mg^{+2} iyonlarının pH 8'in üzerinde molibdenit flotasyonunda olumsuz bir etkiye sahip olduğu bildirilmiştir. Örneğin, pH 11'de pülpe 10^{-2} M $MgCl_2$ ilave edildiğinde molibdenit kazanımı %30 azalmıştır (Hirajima vd., 2016). Molibdenit yüzeyine adsorbe olan $Ca(OH)^+$, $Mg(OH)^+$, $Mg(OH)_2$ gibi hidroksitler ve çökeltiler, alkali ortamda molibdenit kazanımında önemli oranda bir azalmaya yol açarak molibdenit mineralini hidrofilik hale getirebilmektedir (Lu vd., 2019). Molibdenit minerali ile Ca^{+2} ve Mg^{+2} iyonları arasındaki etkileşim mekanizmasının incelendiği bir çalışmada, asidik ortamda molibdenit kenar yüzeyinin (edge surface) oksidasyonu ile $HMoO_4^-$ oluştuğu ortaya konmuştur (Li vd., 2018; Lu vd., 2019). Ca^{+2} ve Mg^{+2} katyonlarının bu kenar yüzeyine adsorbe olmasıyla molibdenitin negatif yüzey potansiyelini azaltmasının veya tersine çevirmesinin mümkün olduğu belirtilmiştir. Bu nedenle, asidik ortamda molibdenit yüzeyi ile hava kabarcığı arasındaki itme kuvveti azalarak molibdenit kazanımının artabileceği vurgulanmıştır (Yi vd., 2021).

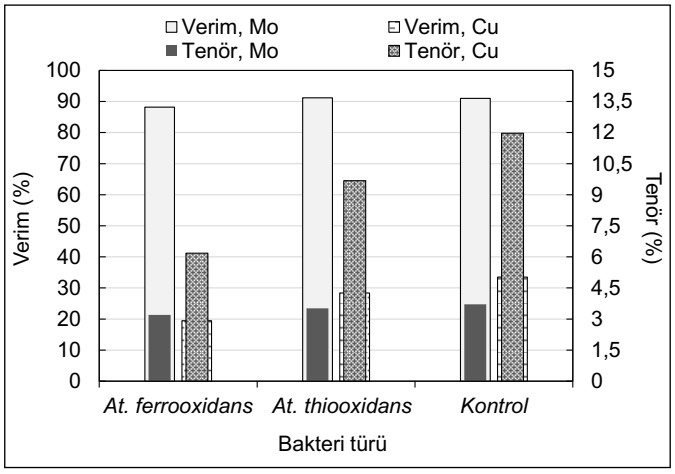
Alkali ortamda $Ca(OH)^+$ ve $Mg(OH)^+$ gibi metal hidroksit katyonları molibdenit yüzeyine adsorplanabilir. Alkali ortamda $Ca(OH)^+$ ve $Mg(OH)^+$'nın molibdenit yüzeyine adsorpsiyonu, fiziksel etkileşimin yanı sıra Ca^{+2} ve Mg^{+2} iyonlarının molibdenit kenar yüzeyinde MoO_4^{-2} ile kimyasal etkileşimi ile gerçekleşebilir (Laskowski vd., 2019; Lu vd., 2019). Ortam pH'sının artışıyla molibdenit minerali yüzeyine adsorplanan metal hidroksit katyonlarının miktarının arttığı ve yüksek pH değerlerinde molibdenit yüzeyinde $Mg(OH)_2$ ve $CaCO_3$ çökeltilerin bulunduğu ortaya konmuştur (Wan vd., 2017; Lu vd., 2019).

Yapılan kimyasal ve mineralojik analizlerde (Çizelge 1 ve Şekil 2) cevher içerisinde kalsit ve dolomit minerallerinin olduğu belirlenmiştir. Biyoflotasyon deneylerinde yüksek asidik (pH 2-2,5) ortamda kalsit ve dolomit minerallerinden açığa çıkan Ca^{+2} ve Mg^{+2} iyonlarının alkali ortamda (pH 10) oluşturabilecekleri $Ca(OH)^+$, $Mg(OH)^+$ gibi kompleks iyonların molibdenit yüzeyine adsorblanmalarıyla ve/veya molibdenit yüzeyine $Mg(OH)_2$, $Ca(OH)_2$ bileşiklerinin çökelmesiyle molibdeniti hidrofilik hale getirerek molibdenit kazanımını önemli bir oranda azaltabilecekleri düşünülmüştür. Bu nedenle, Ca^{+2} ile Mg^{+2} katyonları ve $Ca(OH)^+$ ile $Mg(OH)^+$ iyonlarının oluşmasını azaltmak/engellemek amacıyla sonraki biyoflotasyon deneyleri, bakterilerin faaliyetlerini de olumsuz etkilemeyecek şekilde hafif asidik (pH 5-6) ortamda yapılmıştır (Şekil 7 ve 8).

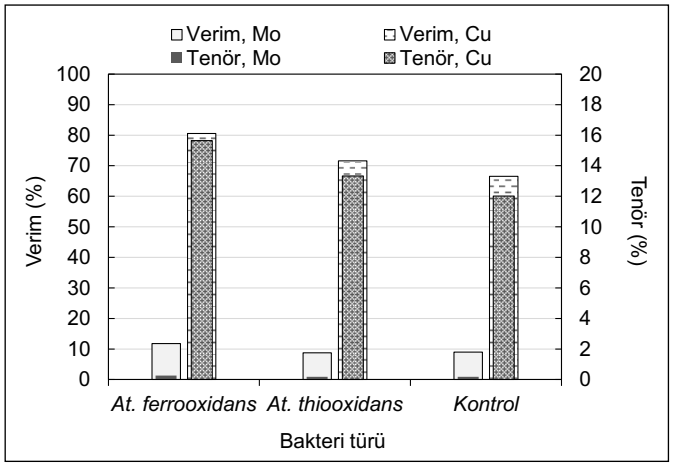
Pülp ortamında ayrıca, bakır minerallerinin çözünmesiyle Cu^{+2} ve Fe^{+3} katyonları da bulunabilmektedir. Yang vd. (2019), pH 4,2'de pülpte Cu^{+2} iyonu derişimi 50 mg/L'ye artırıldığında molibdenit kazanımının %42'den %12'nin altına düştüğünü belirtmişlerdir. Ayrıca, Cu^{+2}'nin bastırma etkisinin pH 2-5 aralığına göre pH 5-8,4 aralığında daha fazla olduğu bildirilmiştir (Yang vd., 2019). Asidik ortamda Cu^{+2} iyonunun ve alkali ortamda oluşan $Cu(OH)_2$ bileşiğinin molibdenitin bastırılmasına neden olabildiği belirtilmiştir (Yi vd., 2021). Bu bakımdan, uzun bakteriyel kıvamlama sürelerinde kalkopiritin oksidasyonu sonucunda pülpte Cu^{+2} iyonlarının bulunması ve derişiminin artması muhtemeldir. Bu da yukarıda açıklandığı üzere molibdenitin hidrofobikliğini azaltmış olabilir. Bu nedenle, sonraki biyoflotasyon deneyleri daha kısa kıvamlama süresinde (30 dk) gerçekleştirilmiştir. Bu deneylerden elde edilen sonuçlar Şekil 7 ve 8'de sunulmuştur.

Bakteriyel kıvamlama süresi olarak 30 dakikanın uygulandığı pH 5-6 aralığında yapılan biyooksidasyon deneylerinde molibdenit konsantresinde %88'in üzerinde Mo verimi elde edilirken, Cu verimi ise %19,5-28,4 arasında değişmektedir (Şekil 7). Fe-oksitleyici At. ferrooxidans ile yapılan deneyde kontrol amaçlı

(bakterisiz) deneylere göre Mo verimlerinde yaklaşık %3 azalma olmasına rağmen, Cu veriminde belirgin bir azalmanın (~%14) olduğu görülmektedir. S-oksitleyici At. thiooxidans ile yapılan deney sonuçlarından, bu bakterinin kalkopirit mineralini bastırma performansının düşük olduğu görülmektedir (Şekil 7 ve 8). At. ferrooxidans kullanılarak pH 5-6 aralığında yapılan biyoflotasyon deneyi sonuçlarından, kontrol deneyine göre molibdenit konsantresinin Mo içeriği daha düşük (%3,71'den %3,2'ye) olsa da Cu içeriğinin de önemli oranda azalmış (%11,97'den %6,18'e) olduğu görülmektedir.



Şekil 7. *Bakteriler ile pH 5-6 aralığında 30 dk kıvamlama sonrası flotasyonda molibdenit konsantresinin tenör-verim değişimi*



Şekil 8. *Bakteriler ile pH 5-6 aralığında 30 dk kıvamlama sonrası flotasyonda kalkopirit konsantresinin tenör-verim değişimi*

3. Sonuçlar

Bu çalışmada, sülfürlü bakır-molibden cevherinden elde edilen toplu Cu-Mo konsantresi üzerinde biyoflotasyon deneyleri yapılmıştır. Deneylerde At. ferrooxidans ve At. thiooxidans türü bakteriler kullanılmıştır. Pülp pH'sı, bakteri türü ve kıvamlama süresinin toplu Cu-Mo konsantresinin biyoflotasyonuna etkileri araştırılmıştır. pH 2-2,5'te yapılan biyoflotasyon deneylerinden elde edilen sonuçlar, molibdenit minerali ile kalkopirit mineralinin benzer bir dağılıma sahip olduğunu göstermiştir. Benzer şartlarda bastırıcı olarak $Na_2O_5S_2$ ve NaCN ile yapılan klasik seçimli flotasyon deneylerinde de molibdenitin hidrofobikliğinin önemli oranda azaldığı belirlenmiştir. Düşük pH'da (2-2,5) molibdenit mineralinin hidrofobikliğindeki azalmanın asidik ortamda çözünmüş iyonların (Ca^{+2}, Mg^{+2} vb. gibi) etkisiyle olabileceği değerlendirilmiştir. Daha yüksek pH'larda (5-6) yapılan biyoflotasyonda ise seçimli olarak molibdenit ve kalkopirit minerallerinin kazanılabileceği belirlenmiştir. At. ferrooxidans kullanılarak yapılan biyoflotasyon deneyleri sonucunda, %3,2 Mo tenörlü %88,2 verimle bir molibdenit konsantresi ve %15,65 Cu tenörlü %80,6 verimle bir kalkopirit konsantresi üretilmiştir.

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