



## Flotation of oxidized antimony ore of Sefidabeh mine

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### Keywords

Stibnite

Oxidized antimony ore

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### Abstract

The main and economic mineral of antimony is stibnite or antimony sulfide, and the research and processes in the world are based on it, and oxide minerals are not considered among the economic and important reserves of antimony due to the difficulty of processing and the lack of optimal efficiency of the flotation method. On the other hand, taking into account that a large part of the antimony reserve of Sefidabeh is made up of low-grade oxidized ore; this research on the method of economic extraction and the possibility of recovering this type of reserve will be important due to the strategic nature of antimony metal. According to the experiments conducted in this research, the effective parameters for flotation include: pH, collector concentration, activator concentration, depressant concentration, activator type, and humic acid concentration. DX7 software was used for statistical modeling of experiments. Based on the above parameters, the design of the experiment was carried out using a partial factorial method and finally the number of 16 experiments was determined for the effect of the above factors on the grade and weight recovery of the sample. Antimony ore flotation with a grade of 4.32% was carried out in a two-stage method. In this method, in the first stage, flotation of antimony sulfur (stibnite, Sb<sub>2</sub>S<sub>3</sub>) was performed at a specific pH by adding the activator of copper sulfate or lead nitrate and the depressant together, potassium amyl xanthate collector and MIBC. In the second stage of flotation, the tailings of the first stage of flotation for antimony oxides were treated with a sodium oleate collector (with determined concentrations) at a specific pH by adding copper sulfate or lead nitrate activator, sodium oleate collector and humic acid and MIBC frother agent. The interaction between pH and activator concentration (BD) has a direct effect on the amount of concentrated antimony, with an increase in pH from 6 to 8 antimony when using an activator concentration of 300 g/t, and a decrease when using an activator concentration of 500 g/t. Flotation was done. In the best conditions, with two-stage flotation of antimony, 68.99% recovery and 13.32 grade were obtained.

## 1. Introduction

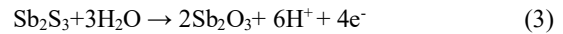
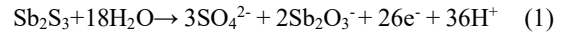
Antimony is used in white metal, which is any of a group of alloys having relatively low melting points. White metal usually contains tin, lead, or antimony as the chief component (e.g., the alloys Britannia and Babbitt). Antimony is used as a hardening alloy for lead, especially in storage batteries and cables, bearing metal, type metal, solder, collapsible tubes and foil, sheet and pipe, semiconductor technology, and pyrotechnics. It is also used in thermoelectric piles, and for blackening iron or coatings. Antimony-containing compounds are used in materials for refrigerators,

air conditioners, aerosol sprays, paints, and flame proofing agents. Approximately half of the antimony used in the United States is recovered from lead-based battery scrap. Antimony is also used medicinally (e.g., antimony potassium tartrate as an emetic and antimony as an antiparasitic agent) [1]. Antimony is a chalcophilic element; therefore, it is found in sulfide veins along with sulfur-friendly elements such as AS, Hg and Ag. The main mineral of antimony is stibnite, which contains 71% of antimony metal [2]. Stibnite is stable at low to medium pH under reducing

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conditions and in the presence of sulfur and is oxidized under surface conditions and forms antimony oxides [5]. Figure 1 shows the range of Eh and pH in which sulfides, oxides and hydroxides of antimony are stable. In the white antimony deposit, stibnite minerals in the oxidant environment have caused the formation of antimony oxide and hydroxide minerals around the stibnite veins. The results of microscopic studies, electron microscopy analyses and BSE images confirm the transformation of stibnite mineral into oxide and hydroxide antimony minerals in this deposit. This transformation, which mainly started from the edge of the crystals and progressed in some samples, eventually leads to the release of sulfur around the antimony minerals. According to the results of electron microscopic analysis which can be seen in Table 1, antimony oxides can be valentinite or cinnarmontite. The chemical formula of both mentioned oxides is  $Sb_2O_3$  and the only major difference between these two minerals is their crystallization system. The crystallization system in valentinite is orthorhombic and in cinnarmontite it is cubic [6]. Other minerals obtained from disintegration of sulphide stibnite

mineral under oxidizing conditions in the region include antimony hydroxides such as stibconite and antimony-calcium hydroxides. Based on the results related to the point analysis of these secondary minerals, stibconite always contains some calcium in its structure. Also, its formula is written as  $Ca_xSb^{(v)}_{2-x}(O, OH, H_2O)_{6-7}$  and  $(Sb)^{III}$  [7]. The reaction of stibnite to antimony oxides and hydroxides is described as follows:



Reaction 1 shows the conversion of stibnite to antimony oxides (valentinite), reaction 2 shows the conversion of antimony oxide to antimony hydroxide and reaction 3 shows the direct conversion of stibnite to antimony hydroxide [8]. The results obtained from the electron microscopy study show the amount of sulfur around these antimony oxide and hydroxide minerals and ultimately the release of sulfur.

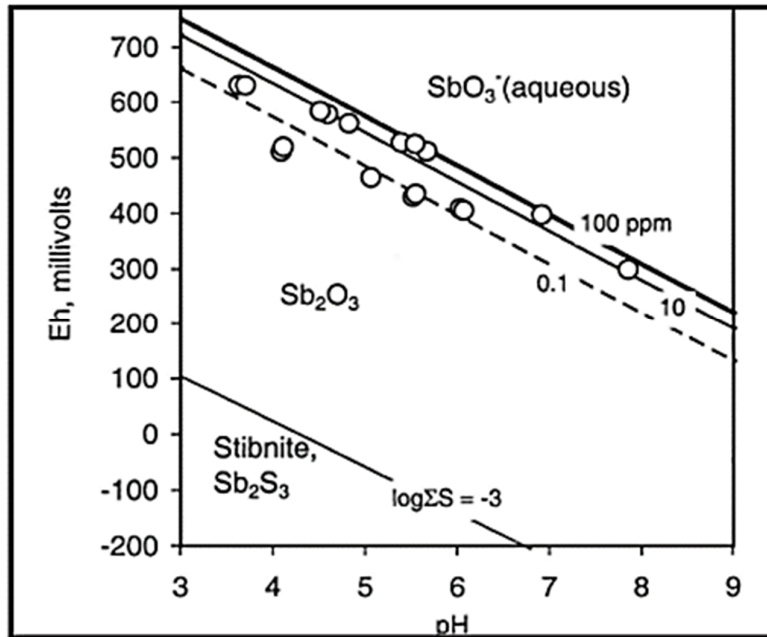


Figure 1. Range of stability of sulfides, oxides and hydroxides of antimony.

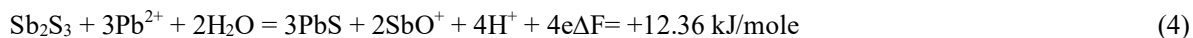
Table 1. The results of the electron microanalysis of the samples of the white antimony deposit.

Sample	SA6a	SA6b	Sample	SA6a	SA6b
S (wt%)	98.49	91.32	S	2.8484	3.0618
Sb	0.49	4.26	Sb	0.0350	0.0040
Fe	0.17	0.11	Fe	0.0020	0.0030
Total	99.15	95.69			

Antimony oxide minerals are often processed by gravity separation and flotation. Gravitational separation is an old method used to separate light and heavy mineral particles in mineral processing. Gravity separation equipment is still used as a rougher concentrate unit in the processing of coal, iron ore, gold, barite, tin and tungsten. The selected method in gravity separation called Cross belt chute has many advantages, but its results are very limited in the separation of antimony oxide minerals [9]. The separation process by gravity method only leads to good recovery of large particles of antimony oxide minerals. This method causes problems for particles in the range of soft and super soft antimony oxides. To solve this problem, some researchers developed a method that is a combination of gravity methods that include centrifuges that include Belt chute gapi and Vibration belt chute [10]. Zhang et al. processed an antimony oxide mineral using a belt chute combined with gravity method in guanxi dujie, and the separation results were poor [11]. This shows that the ability of gravity methods to separate antimony oxide minerals is very limited. Gülcan et al. found that heavy medium separation is the only method that can be used for stibnite ore. Therefore, four samples with 10, 12, 14 and 16 percent grade were tested. They showed when the concentrate grade is between 10 and 16%, the recovery of the

total concentrates will be between 46-49% if the feed grade was 1.18% antimony and the feed rate was 20 tons per hour [12]. However, many of these new technologies are still in the laboratory stage and it takes time to enter the industry.

After the invention of the flotation method, the use of the gravity separation method was reduced. Because flotation is more effective for a wide range of minerals, including antimony oxide minerals. The flotation of antimony oxide minerals is affected by complex compounds and the low buoyancy of antimony oxide, which makes only one flotation process difficult to achieve a good result. Deng et al. [13] investigated the effect of  $Mn^{2+}$  for antimony mineral flotation behavior. They showed that  $Mn^{2+}$  can activate antimony minerals and improve the separation of antimony oxides and materials. But recovery does not improve flotation and does not speed up the flotation process. The use of  $Mn^{2+}$  as an activator, fatty acid as a collector and water glass as an inhibitor for the processing of antimony minerals with a grade between 1.9 and 2% leads to a concentrate with an antimony grade of 17% to 19% and a recovery rate of 70% to 74%. Solozhenkin et al. investigated the use of copper and lead metal ions as antimony activators. This study showed that by adding lead nitrate to the pulp, antimonite is activated and lead sulfide is formed on its surface:



With the activation of antimony, the ratio of S to Pb grows from 1.88 to 1.96. Copper cations also activate antimony in  $Sb_2S_3$ , so S to copper increases from 1.88 to 2.55. From the comparison of these ratios, it is clear that copper behaves more intensely in the behavior of activating antimony from the crystal network. Solozhenkin et al. showed that at a copper or lead concentration of 10 mg / L, Sb / Cu is 5.7 more than Sb / Pb [14]. A sulfide-oxide-composite antimony ore from Xikuangshan was studied by Chen et al. [15] using a flotation-sulfidation-reflotation process. At first, a conventional flotation was used to recover antimony sulfide mineral. The flotation residue was drained and dried, and 1 to 2% of salt was added to it as a chlorine agent and charcoal as a reducing agent at a temperature of 960 degree Celsius and 20 minutes. Then the flotation is done again, and finally the mixed concentrate of antimony with 8.7% antimony grade and 95.01% recovery is obtained. Pang et al. [16] studied oxydmon minerals including ceroantiite from

Yunnan using gravitational separation tests. Their tests included separation for the processing of oxidized minerals using 5% sodium chloride as a chlorinating agent and 1.5% pulverized coal as a reducing agent under a temperature of 30 degree Celsius - heating to 96 degrees Celsius with a heating time of 30 minutes. The results of these tests were antimony concentrate with a grade of 71.56% and a recovery of 50.53%. Peng et al., who performed an analysis of Cervantes from Yunnan, used gravitational separation tests. Their tests included separation to process antimony oxide mineral using 5% sodium chloride as a chlorinating agent and 1.5% powdered charcoal as a reducing agent under a temperature of 960 degrees with a heating time of 30 minutes. The results of these tests were antimony concentrate with a grade of 71.56% and a recovery of 50.53%). New research is mainly oriented towards the development of flotation reagents. Wang et al. [17] studied the effect of sodium dodecyl sulfate (SDS) and  $Cu_2$  on the flotation of cervantite. The results showed that

for a certain range of pH, copper ions activated the flotation of cervantite., especially when sodium dodecyl sulfate was used as a flotation collector. When the pulp pH was between 6 and 8, the antimony recovery rate reached more than 80%, while SDS had no capacity to collect antimony when no copper ions were added. They also studied the chemistry of flotation solution in the activation mechanism of copper ions.  $\text{CuOH}^+$  was found to be the main active agent in the flotation of cervantite. The adsorption of  $\text{OH}^-$ ,  $\text{Cu}^{2+}$ ,  $\text{CuOH}^+$  and SDS on the surface of cervantite. was studied using the density functional theory. The results showed that the use of copper ion as an activator and SDS as a collector resulted in a recovery rate for cervantite. of more than 90% when the pH was between 6 and 8. Energy absorption for different adsorbents on cervantite surfaces decreases from  $\text{Cu}^{2+}$ , SDS,  $\text{OH}^-$ , and  $\text{CuOH}^+$  respectively. SDS is chemisorbed on  $\text{CuOH}^+$ . Wang et al. reported that the pH of the pulp must be very acidic (pH < 2) or very alkaline (pH > 10.5) to separate cervantite from quartz. However, fine-tuning pulp pH under acidic conditions on a practical scale is a challenge because the ore is alkaline and economically infeasible. Butyl ammonium

Aerofloat, in particular, has been reported as the most widely used reagent among the Aerofloat types in China due to its selectivity and collecting ability [18]. Wu et al. [19] recently reported the successful development of a collector referred to only as 5# oil to be used as the only collector along with lead nitrate (activator) for stibnite flotation. The presence of friable clay minerals such as kaolinite and illite can also contribute to the generation of undesirable slimes that increase the viscosity of the pulp and make it difficult to float stibnite [19]. In this study the effective parameters for flotation include: pH, collector concentration, activator concentration, depressant concentration, activator type, humic acid concentration on antimony oxide mineral.

## 2. Materials and Methods

In this study Sefidabeh antimony mine ore was used for processing. Mineralization in Sefidabeh antimony deposit has been done in the form of veins along the main faults of the region. Figure 1 shows the mineralization of antimony in the form of veins in the Sefidabeh antimony deposit.



Figure 1. Antimony mineralization in the form of veins in Sefidabeh antimony deposit. [3].

The main antimony mineral in Sefidabeh antimony deposit is stibnite with the chemical formula  $\text{Sb}_2\text{S}_3$ ; which has filled the fractures in the form of veins. Elongated and needle-like crystals

of stibnite with bright shiny surface, metallic luster and lead gray color can be seen well in the hand sample in the white antimony deposit. Figure 2 shows the characteristics of this deposit.



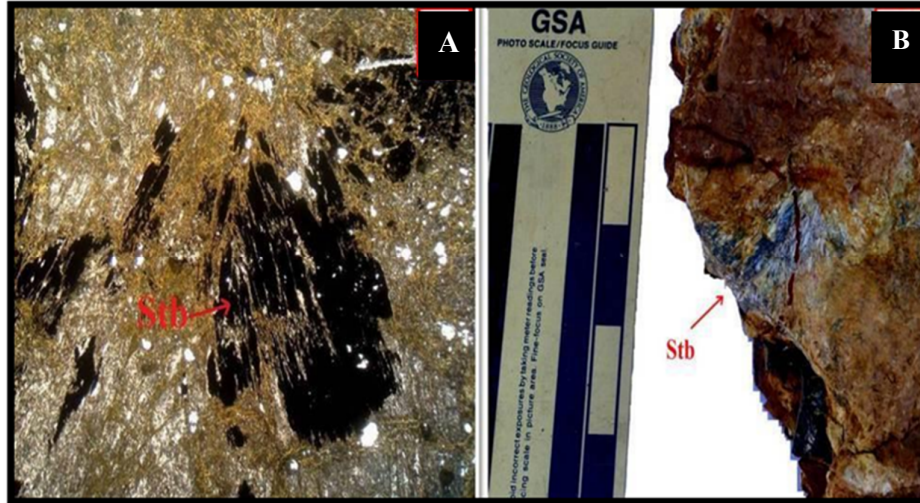


Figure 2. Stibnite mineral profile in Sefidabeh antimony deposit. A) Stibnite needle minerals in the hand sample. b) Microscopic section of needle-shaped stibnite crystals with radial texture. The width of the field of view is 2 mm (XPL).

### 3. Geographical location

Sefidabeh antimony deposit is located on the northern border of Sistan and Baluchistan province and the southern border of South Khorasan province; this area is located in the eastern part of Lut desert. The geographical location is located 220 km north of Zahedan, 150 km northwest of Zabol and 75 km from Sefidabeh village.

The coordinates of one of the deposit points are as follows:

N 30° 46' 26"

E 60° 05' 41"

The topographic map of Sefidabeh antimony deposit area 1:500,000 west of Butgo, sheet number IV 8051 of the Army Geographical Organization, as well as the geological quadrangle 1:250,000 of Hamon Lake and sheet 1:100,000 of Sastregi mountain.

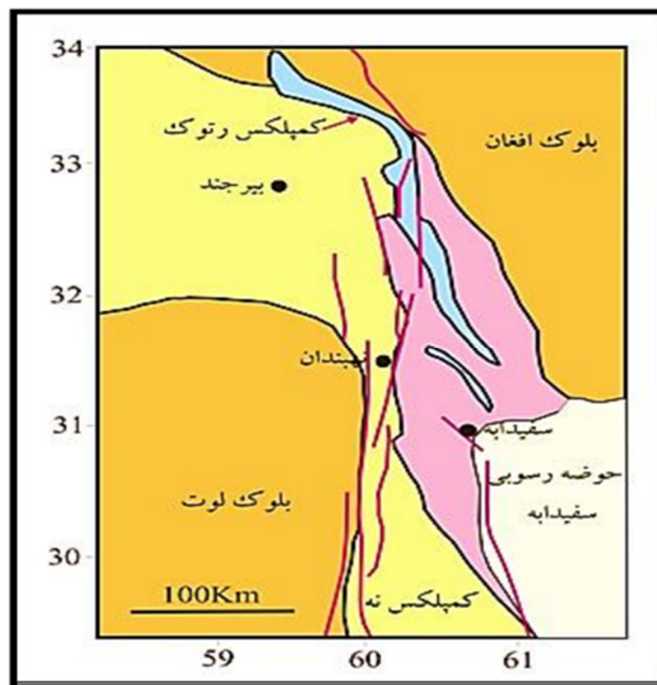


Figure 3. Location of the structural state of Sefidabeh village [4].

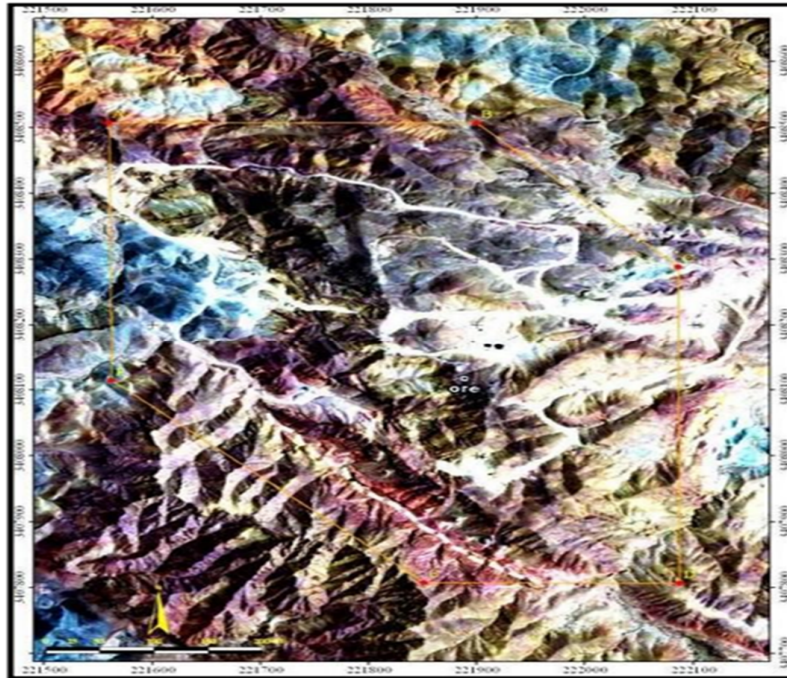


Figure 4. Satellite image of the study area where the location of the deposit is marked with a dashed line.

**4. Sample preparation**

In order to carry out the desired tests of this project, 50 kg of crushed samples from the output of the ball mill unit were sent to Kashan University by Sefidabeh antimony mine. This sample was first

divided into smaller sub-samples in a conical form and coded and archived at each step of the witness sample. The particle size distribution analysis of shipping materials is shown in Table 2 and Figure 6.

**Table 2. particle size distribution analysis of antimony samples.**

Screen number (mesh)	Dimensional range (µm)	Cumulative percentage remaining	Cumulative passing percentage
150	+106	14	86
200	-106+75	20.6	79.4
230	-75+63	25.5	74.5
270	-63+54	28.4	71.6
400	-54+38	36.5	63.6
500	-38+25	42.9	57.2
Pan	-25	-	-
	sum		

$d_{80}=78 \mu\text{m}$

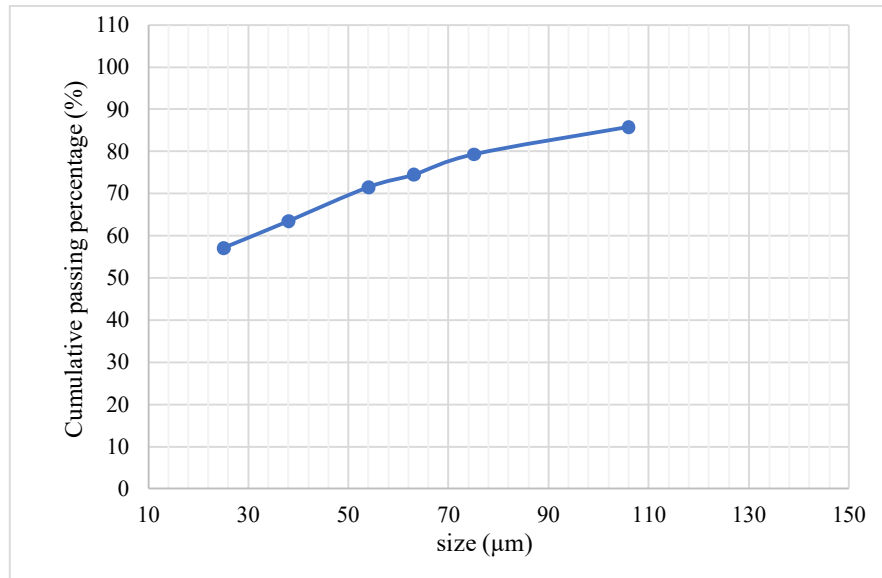


Figure 6. Granulation curve of antimony feed sample.

According to the size distribution of the sample, it can be seen that the  $d_{80}$  of the sample is about 78 micro meter. Also, 57% of the particles in the sample are smaller than 25 micro meter.

#### 4.1. Results of X-ray Diffraction (XRD) studies

In order to identify the minerals in the ore, an X-ray diffraction analysis was performed on the powdered sample. The results of this test are shown in Figure 7. As it is clear from the figure, quartz and 5-valent antimony oxide are present.

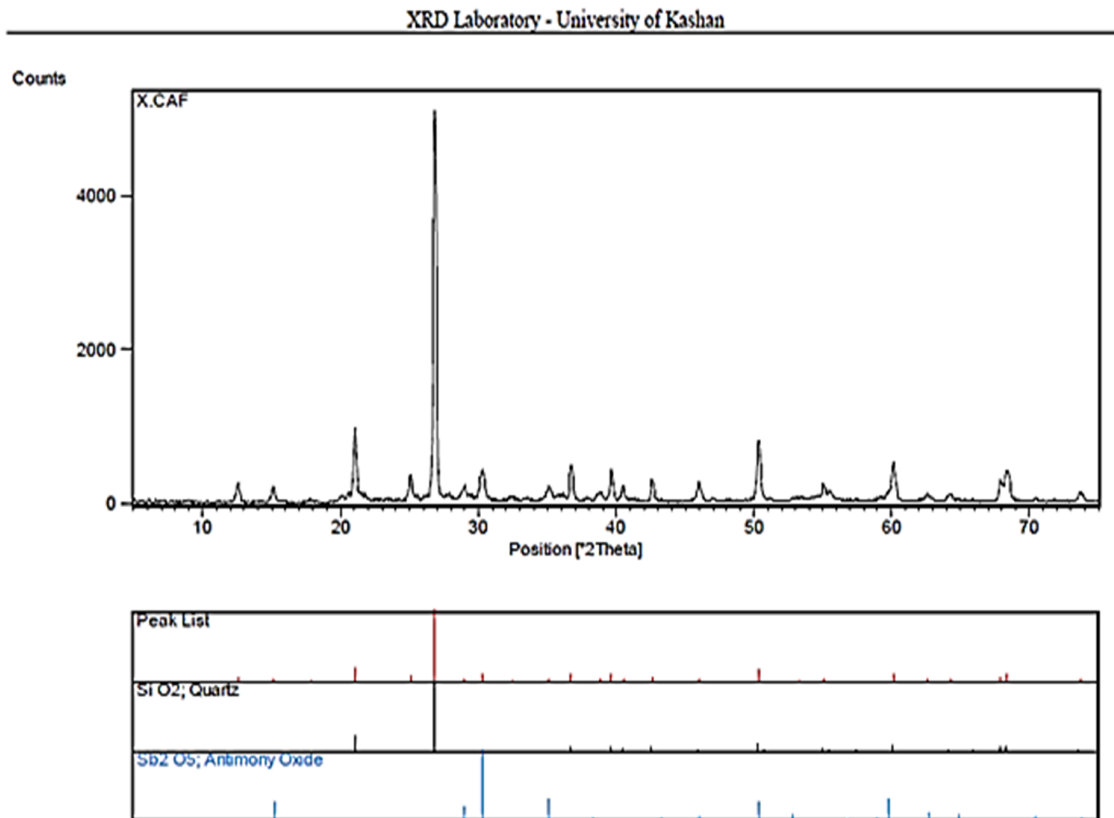


Figure 7. Analysis results (XRD) of Sefidabeh antimony ore sample.

The formation of antimony minerals largely depends on its 3+ or 5+ oxidation state. As Figure 7 shows, the antimony present in SefidabehSefidabehh mine ore is more 5-valent antimony and its flotation is more difficult than 3-valent antimony. Pentavalent antimony can be reduced to trivalent antimony by magnetite and iron sulfide, and trivalent antimony is not reduced either. On the surface of magnetite, trivalent antimony forms an absorption complex with high symmetry. As the pH of antimony increases, it may decrease. When the environmental pH values are more than 6.5, pentavalent antimony is reduced to trivalent antimony within 30 days. On the other hand, on the surface of iron sulfide, even in a wide

range of antimony pH 5, it is completely reduced within one hour. This reaction occurs only on the surface of minerals, which indicates the surface iron and antimony 5 oxidation reduction reaction, so sulfides are not involved.

**4.2. XRF analysis results**

In order to identify the elements, present in the ore, an XRF analysis was performed on the powdered primary sample. The results of this test are shown in Table 3. As it is clear from the table, the amount of antimony in the sent sample is 4.32% and the main silica content is 74.1%.

Table 3. Analysis of samples sent from Sefidabeh antimony mine for flotation

Element	SiO2	BaO	CaO	Fe2O3	K2O	MgO	MnO	P2O5	SO3	TiO2	Cu	Pb	Zn	Sr	Sb	LOI
	74.1	0.20	1.20	5.2	1.13	0.76	0.12	0.21	1.40	0.60	<	0.06	<	0.14	4.32	6.82

**4.3. Report of microscopic studies**

Three fractions were done for microscopic studies. For this study, fractions of +74, +54, +37 microns were selected.

**4.3.1. Fractions of +74 microns**

Pieces with different composition and size can be seen in the cross-section prepared from this fraction. Silica in the form of microcrystalline and less coarse and polycrystalline particles accounts for more than 50% of the constituents. Most of the siliceous parts are stained and mixed with iron oxide-hydroxides of the type of hematite and fine

and earthy goethite. In addition to silica minerals and iron oxide-hydroxides, less abundant constituents including calcite, clay minerals, particles with the characteristics of realgar-orpiment and illite are also seen. Opaque minerals are present at a maximum of 1 percent by volume, and in about 80 percent of them, they are seen in free form. Minerals with optical characteristics similar to antimony oxide-hydroxides are about 3 times that of sulfide minerals of the stibnite type (based on the study of polished sections) and their degree of freedom is about 10% lower than opaque minerals.

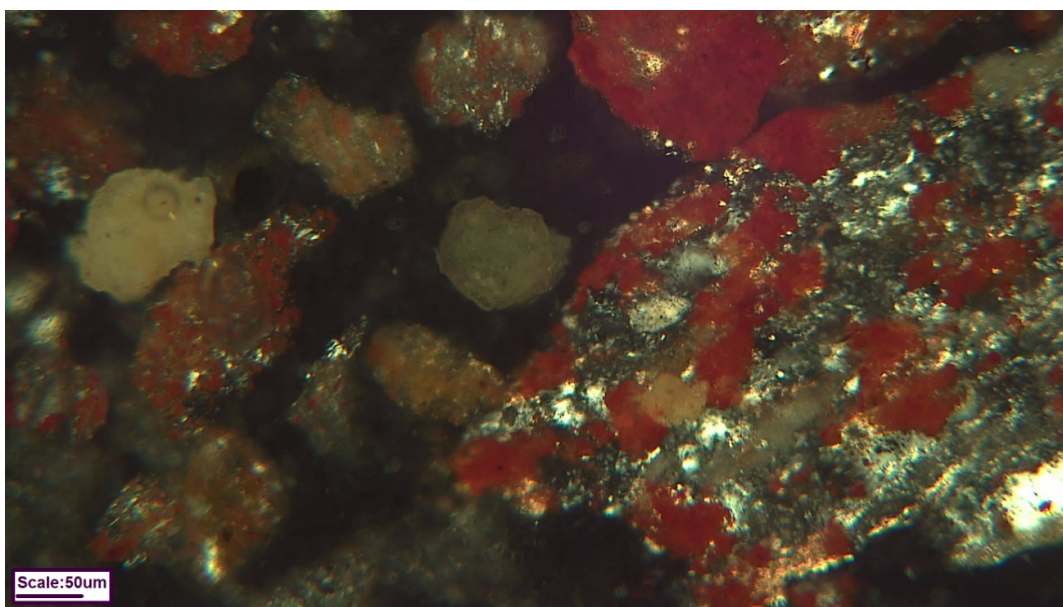


Figure 8. Thin section of Sefidabeh antimony sample in +74-micron fraction.



#### 4.3.2. Fractions of +54 microns

In Figure 8, antimony oxide minerals are cervantite, which is marked with brown color. And the transparent metal minerals are stibnite, which is

marked with crystal color. As you can see in the figure, at this size, the antimony minerals have not reached the degree of liberation.

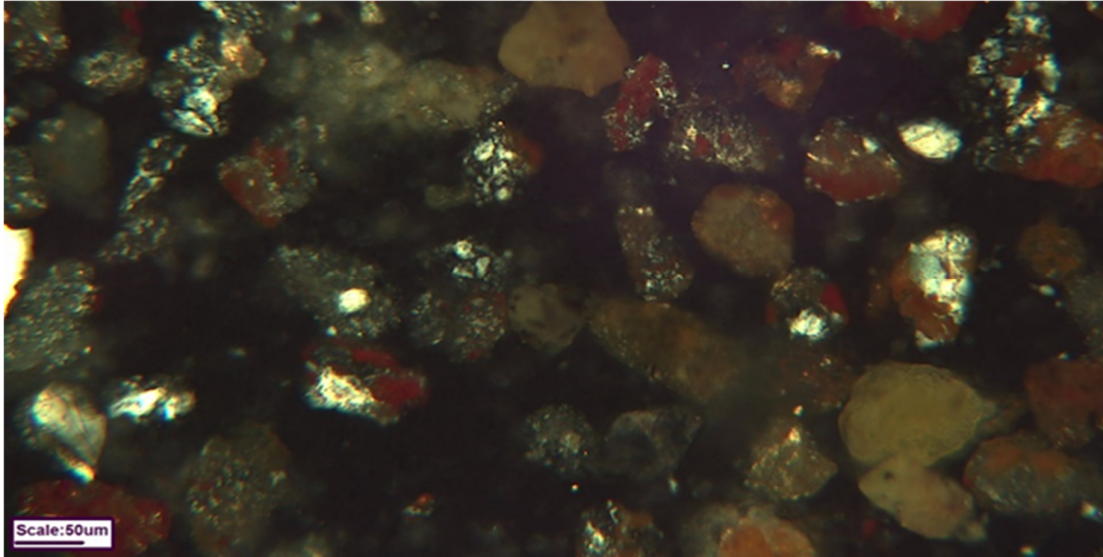


Figure 8. Thin section of Sefidabeh antimony sample in +54-micron fraction.

#### 4.3.3. Fractions of +37 microns

In Figure 9, the antimony oxide minerals are cervantite, which is marked with brown color. The transparent metallic minerals are stibnite, which is

marked with crystal color. As you can see in the figure, at this size, the antimony minerals have not reached the degree of liberation.

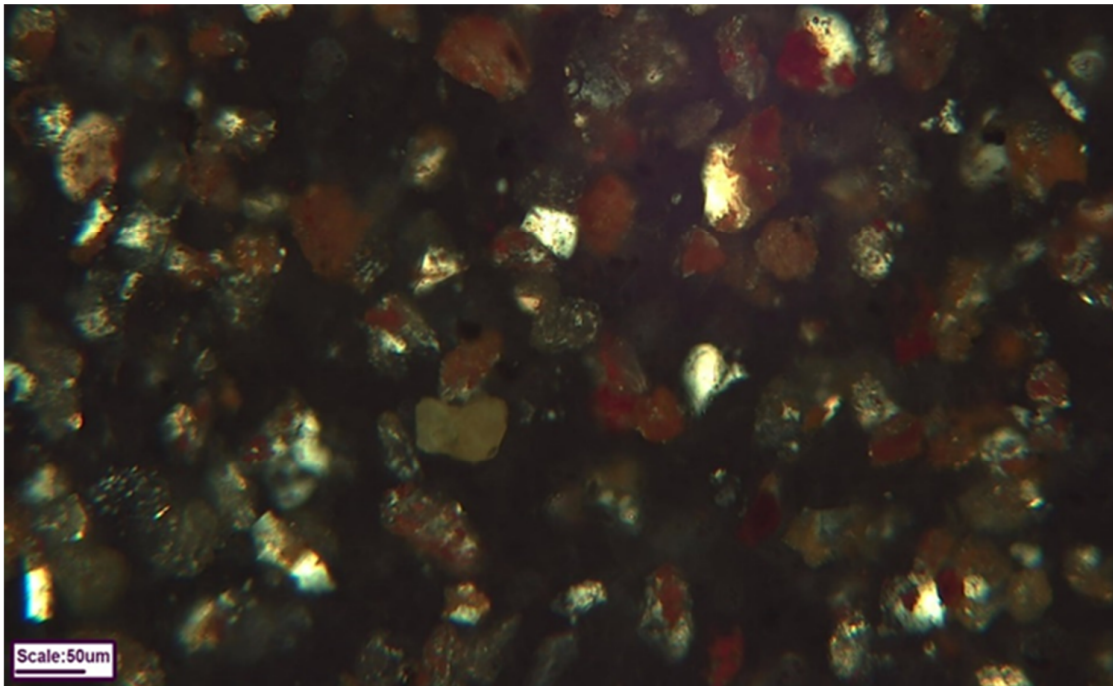


Figure 9: Thin section of Sefidabeh antimony sample in +37-micron fraction.



### 4.3.4. Chemicals and reagents

Chemicals used in this work include sodium oleate and humic acid as collector, copper sulfate and lead nitrate as activator, sodium silicate as depressant and MIBC as frother agent. All chemicals used were of high laboratory purity from Merck.

### 4.4. Test equipments

Denver laboratory cell with a volume of 2 liters was used for flotation tests. Mineral samples weighing 660 grams were used in each experiment. The concentrate was dried by a dryer at 100°C after each test. Denver model pH meter was used to measure pH and hydrochloric acid and lime were used to adjust pH meter. All experiments were performed under the same conditions of 25°C

temperature and 1 atmosphere pressure. The parameters measured in each experiment include: time, pH, concentration of collector and depressant, amount of frother agent.

As shown in Figure 10, the flotation was carried out in two steps. In the first stage, antimony sulfide was floated and then antimony oxide was floated. In the first stage, the activator and sodium silicate are added, which is prepared for 5 minutes, then potassium amyl xanthate with a concentration of 400 g/t is added and prepared for 2 minutes, and the MIBC frother agent is added for 1 minute and added to it is foamed for 4.5 minutes. In the second step, sodium oleate and humic acid collector are prepared for 2 minutes and MIBC frother agent is added for 1 minute and foaming is done for 4.5 minutes.

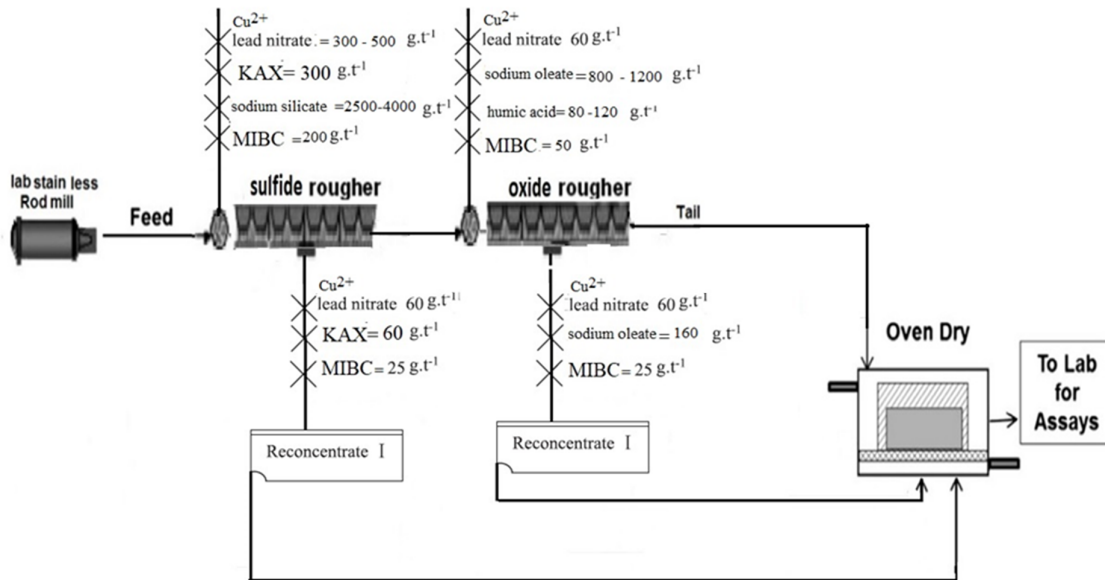


Figure 10. Two-stage flow sheet of antimony ore flotation.

### 4.5. Experiment method

DX7 software has been used for statistical modeling of experiments. As shown in Figure 10. Antimony ore flotation with a grade of 4.32% was carried out in a two-step method. In this method, the first step involves the flotation of antimony sulfur (stibnite, Sb<sub>2</sub>S<sub>3</sub>) at a specific pH achieved by adding a copper sulfate activator or lead nitrate activator, along with a depressant. Potassium amyl xanthate collector and MIBC frother agent are also added. The conditioning times are as follows: 3 minutes for sodium silicate activator and depressant, 2 minutes for the collector, and 1 minute for MIBC. The concentrate is collected for 4.5 minutes, and a cleaner stage is performed on

the collected concentrate. It was done as shown in the flow sheet of Figure 10. After collecting the concentrate for 3 minutes, it was analyzed after dewatering and drying. In the second stage of flotation, the tailings of the first stage of flotation were carried out for antimony oxides with a sodium oleate collector (with determined concentrations) at a specific pH by adding the activator of copper sulfate or lead nitrate, sodium oleate collector and humic acid and foaming agent. MIBC flotation was done (preparation time for activator is 3 minutes, collector is 2 minutes and MIBC is 1 minute) and the concentrate was collected for 4.5 minutes and a cleaner stage was collected on the concentrate. After collecting the concentrate for 3 minutes, the concentrate was analyzed after dewatering and

drying. Table 4 shows the desired parameters for conducting flotation tests and the values of the low

and high levels of each factor. It is worth mentioning the feed rate is 4.32.

**Table 4. Factors and their level values in the design of flotation experiments.**

agents	pH	Collector concentration (g/t)	Activator concentration (g/t)	Depressant concentrate (g/t)	Activator type	Humic acid concentration (g/t)
Low level (-)	6	800	300	2500	Cu <sup>2+</sup>	80
High level (+)	8	1200	500	4000	Pb <sup>2+</sup>	120

Based on the above parameters, the design of the experiment was carried out using a partial factorial method and finally the number of 16 experiments was determined for the effect of the above factors on the grade and weight recovery of the sample. After determining the test conditions using the partial factorial method, all tests were performed using a mechanical flotation device with a rotor rotation speed of 1000 rpm during preparation and 1000 rpm during foaming, in a cell with a volume of 2 Liters. In all experiments, a pulp with a solid percentage of 30% was utilized. Potassium amyl xanthate was used as a sulfide collector, while sodium oleate and humic acid were employed as antimony oxide collectors. Sodium silicate served as an inhibitor. Lime was added to increase the pH,

and hydrochloric acid was used to reduce the pH. Additionally, tap water was utilized for the flotation tests.

## 6. Results and Discussion

Table 5 shows the conditions related to conducting the tests and the answers obtained from them. Flotation was carried out under the following optimum conditions: pH 8, collector concentration of 800 g/t, activator concentration of 300 g/t, depressant concentration of 2500 g/t, Pb<sup>2+</sup> as the activator type, and humic acid concentration of 80 g/t. These conditions resulted in a recovery of 68.99% and a grade of 13.32.

**Table 5. Parameters and responses from flotation tests.**

Test number	pH	Collector concentration (g/t)	Activator concentration (g/t)	Depressant concentrate (g/t)	Activator type	Humic acid concentration (g/t)	Grade (%)	Recovery (%)
1	6	800	300	2500	Cu <sup>2+</sup>	80	14.41	51.46
2	6	1200	500	2500	Pb <sup>2+</sup>	80	13.45	67.98
3	6	1200	300	4000	Cu <sup>2+</sup>	80	14.58	44.18
4	8	800	300	2500	Pb <sup>2+</sup>	80	13.32	68.99
5	6	1200	500	4000	Cu <sup>2+</sup>	120	14.18	53.39
6	8	800	500	2500	Pb <sup>2+</sup>	120	15.14	47.16
7	6	800	500	4000	Pb <sup>2+</sup>	80	13.65	65.32
8	6	800	300	4000	Pb <sup>2+</sup>	120	14.05	56.02
9	8	800	300	4000	Cu <sup>2+</sup>	120	13.81	63.43
10	8	800	500	4000	Cu <sup>2+</sup>	80	14.01	49.17
11	6	1200	300	2500	Pb <sup>2+</sup>	120	14.47	44.77
12	8	1200	300	2500	Cu <sup>2+</sup>	120	13.64	60.47
13	8	1200	500	4000	Pb <sup>2+</sup>	120	14.72	44.60
14	8	1200	300	4000	Pb <sup>2+</sup>	80	13.97	57.05
15	6	800	500	2500	Cu <sup>2+</sup>	120	13.70	60.74
16	8	1200	500	2500	Cu <sup>2+</sup>	80	13.86	58.81

### 6.1. Using potassium amyl xanthate in two-stage flotation

As shown in Figure 10, potassium amyl xanthate (KAX) was used for the first stage flotation, which

is the flotation of antimony sulfide mineral (stibnite) in two-stage flotation. As shown in Table 6, 300 gram per ton was selected for flotation tests.

**Table 6. Factors and their level values in the design of flotation experiments.**

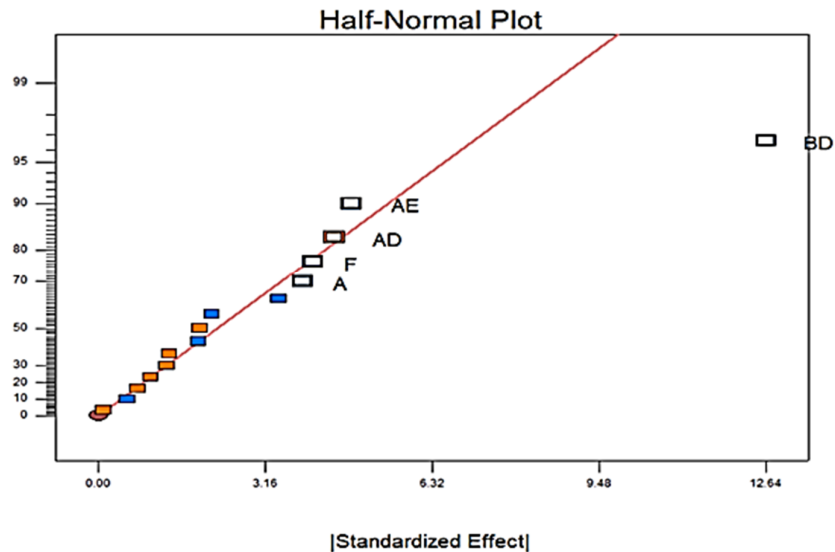
agent	pH	Collector concentrate KAX (g/t)	Recovery (%)
1	7	100	11
2	7	200	15
3	7	300	18
4	7	500	19

**6.2. Statistical investigation of flotation tests with the aim of antimony grade**

According to the desired answers, which include antimony grade and its recovery, the appropriate test design model and the parameters affecting it calculated by the software are observed and checked for each answer.

As in Figure 11, it can be seen that by selecting the factors AE, F, A, AD, BD (AE is the interaction effect of collector concentration and inhibitor concentration, A is collector concentration, F is

humic acid concentration, AD is the interaction effect of collector concentration and active concentration activator, BD interaction effect of pH and concentration of activator) which have the largest influence values, the influence of these factors are scattered and far from the fitting line of the error distribution, and in contrast to the influence of other influences, they are concentrated very close to the fitting line.. As a result of the initial estimation, the factors AE, F, A, AD, BD are obvious factors.



**Figure 11. Semi-normal probability curve to check concentrate recovery.**

According to Figure 12, by choosing the points AE, F, BD, the line related to the error distribution is closer to zero, as a result of the initial estimate that AE, F, BD (AE, the interaction effect of

collector concentration and depressant concentration, F humic acid concentration, BD interaction effect of pH and activator concentration) are obvious factors.

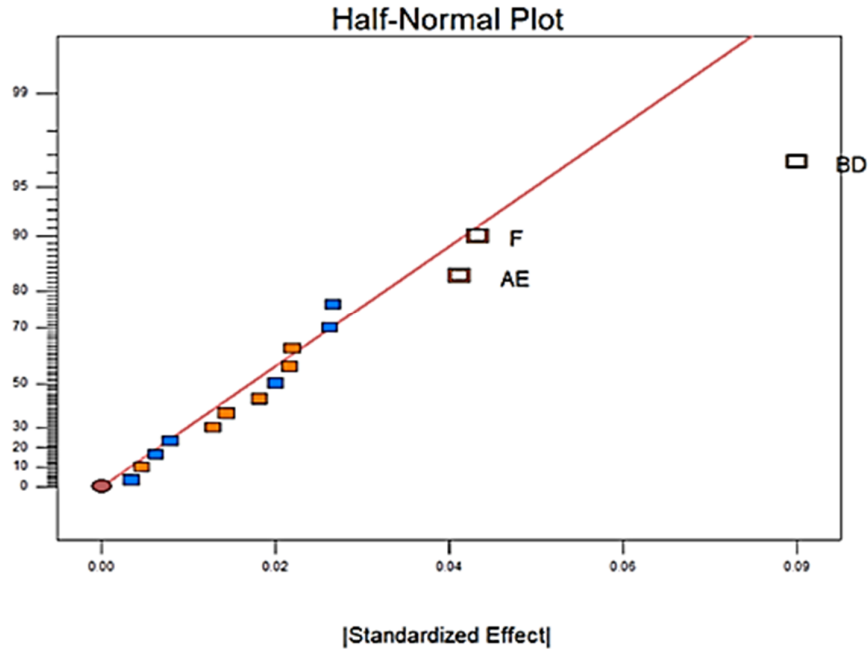


Figure 12. Semi-normal probability curve for antimony concentration check.

According to Figure 13, BD (interaction of pH and concentration of activator) is the most influential parameter on the concentration of antimony, and factors AE and F (F of humic acid

concentration and AE of interaction of collector concentration and depressant concentration) can also have an effect on the grade of antimony concentrate.

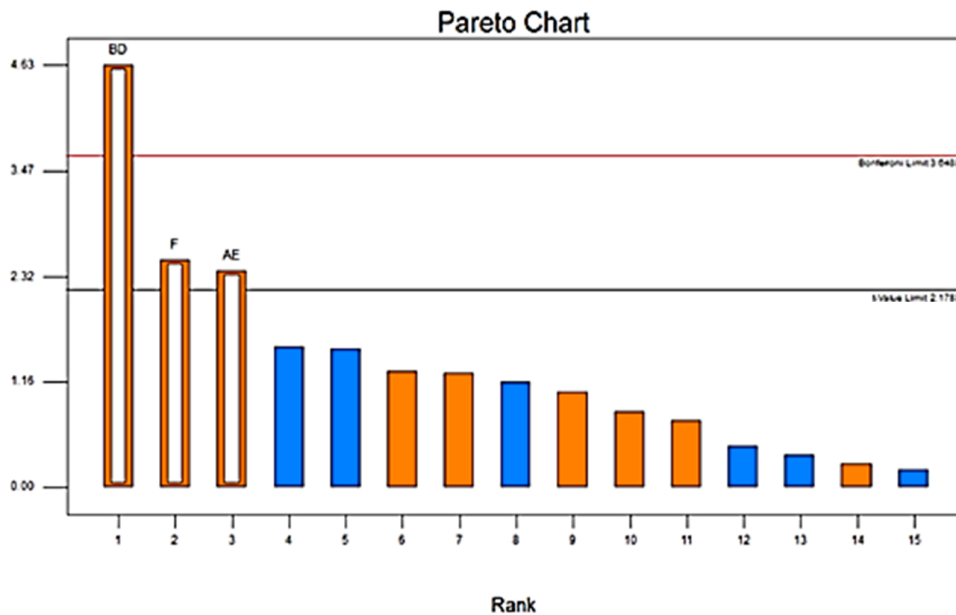


Figure 13. Pareto chart to check the grade of antimony concentrate.

In Table 7, the values related to the analysis of variance of the laboratory data and the effect of the parameters on the concentration of antimony can be seen. As can be seen at the 95% confidence level, three factors of interaction between pH and

activator concentration (BD), humic acid concentration (F), interaction between collector concentration and depressant (AE) were respectively identified as effective factors on the concentration of antimony. Given with these

interpretations, the considered mathematical model has become meaningful. In terms of importance and degree of influence, the interaction factor between pH and activator concentration (BD) was determined to be the most effective factor on antimony titer. After the humic acid concentration (F), the interaction between the concentration of

the collector and the inhibitor (AE) is of secondary importance. However, the rate changes are not very noticeable. Other factors have not had a significant effect on the value of carat. The appropriate mathematical model calculated by considering the coding values of the factors is in the form of equation (5).

$$\text{Grade} = +14.03 + 0.072 * A + 0.020 * B + 0.053 * D + 0.085 * E + 0.17 * F + 0.17 * A * E + 0.32 * B * D \quad (5)$$

**Table 8. Values of the ANOVA page to check the concentration of antimony.**

agents	sum of squares	Degree of liberation	mean sum of squares	Fisher's value distribution (F value)	significant level (P value)	
model	2.85	7	0.41	4.73	0.0221	significant
Collector concentration (A)	0.084	1	0.084	0.97	0.3527	
pH	6.320E-003	1	6.320E-003	0.073	0.7933	
Activator concentration (D)	0.044	1	0.044	0.51	0.4936	
Depressant concentration (E)	0.12	1	0.12	1.35	0.2793	
Humic acid concentration (F)	0.49	1	0.49	5.68	0.0443	
The interaction between the concentration of the collector and the depressant (AE)	0.45	1	0.45	5.21	0.0519	
The interaction between the concentration of the pH and the activator (BD)	1.66	1	1.66	19.31	0.0023	
Remain	0.69	8	0.086			

Figures 14 and 15 are provided to investigate the interactions of AE and BD. As can be seen, two factors of interaction between pH and concentration of activator (BD), interaction between concentration of collector and depressant (AE) have a direct effect on the amount of antimony concentration. Figure 14 shows that the interaction between the concentration of the collector and the depressant (AE) has a direct effect on the amount of concentrated antimony by increasing the amount of the collector from 800 to 1200 g/t. The antimony grade decreases when using the depressant concentration of 2500 g/t and it increases when using the depressant concentration of 4000 g/t depressant.

Figure 15 shows that the interaction between pH and activator concentration (BD) has a direct effect on the amount of concentrated antimony, with an

increase in pH from 6 to 8 antimony when using an activator concentration of 300 g/t., it decreases and when using the concentration of the activator, it increases by 500 g/t. As known from the literature, the addition of lead nitrate in the flotation of antimony ores improves the flotation conditions at 6.5 pH and more than 89% of the added lead is adsorbed on the antimony ores surface as Pb<sup>2+</sup> ions. Pb<sup>2+</sup> adsorption on the negatively charged antimony ores surface causes an increase in the zeta potential of antimony ores. Studies have shown that this effect depends on the amount of added Pb(NO<sub>3</sub>)<sub>2</sub> and is an optimum value. For this reason, experiments were carried out to determine the optimum amount of Pb Nitrate. Then antimony grade increased in an activator concentration of 500 g/t., but it decreased in an activator concentration of 300 g/t.



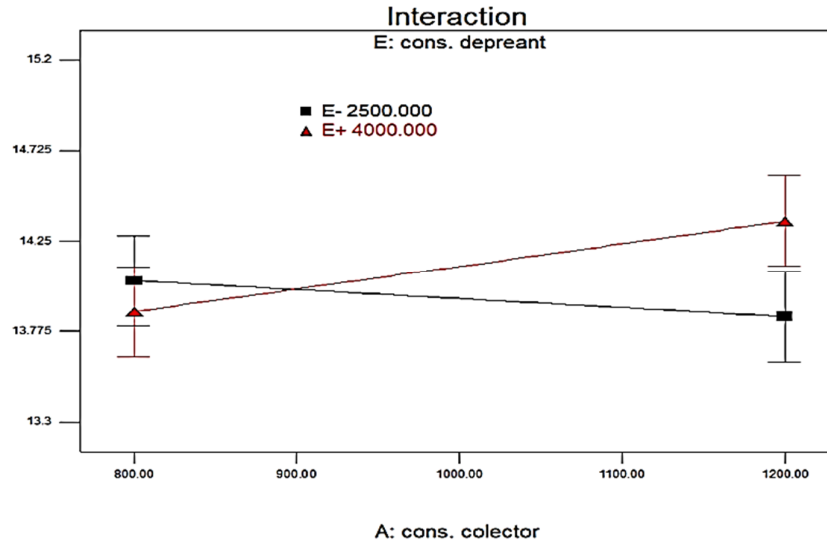


Figure 14. Graphic representation of the interaction of AE on antimony grade.

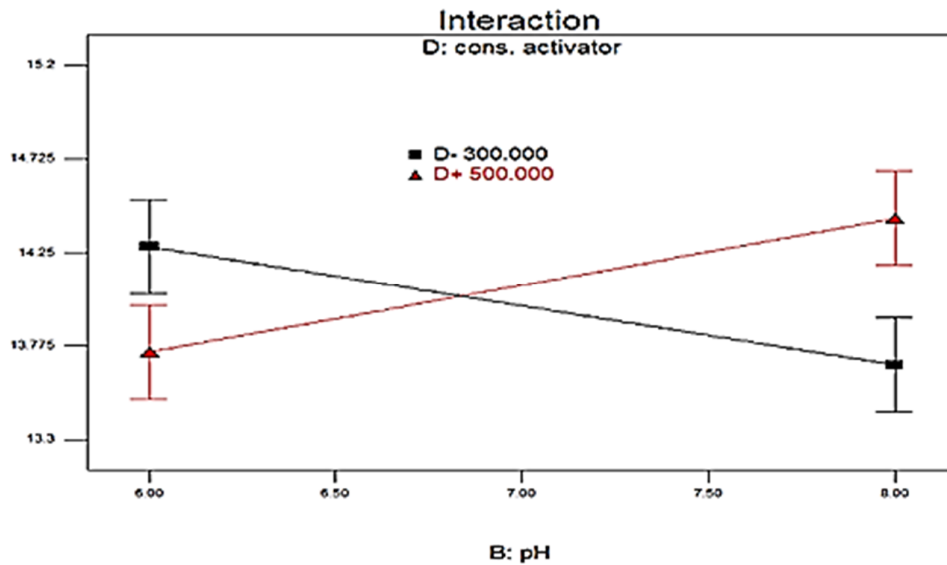


Figure 15. Graphic representation of the interaction of BD on antimony grade.

Figure 16 shows that the concentration of humic acid (F) has a direct effect on the amount of antimony in the concentrate, increasing the concentration of humic acid from 80 to 120 antimony. The humic acid has influences on removal process of aqueous heavy metals. Humic acid tends to be adsorbed on various mineral

colloids, which affects the transport of mineral colloids and the pollutants they adsorbed [20]. It has been reported that a high concentration of humic acid prevents or delays the transition of Fe (III) in a mineral phase with low crystallization [21,22].

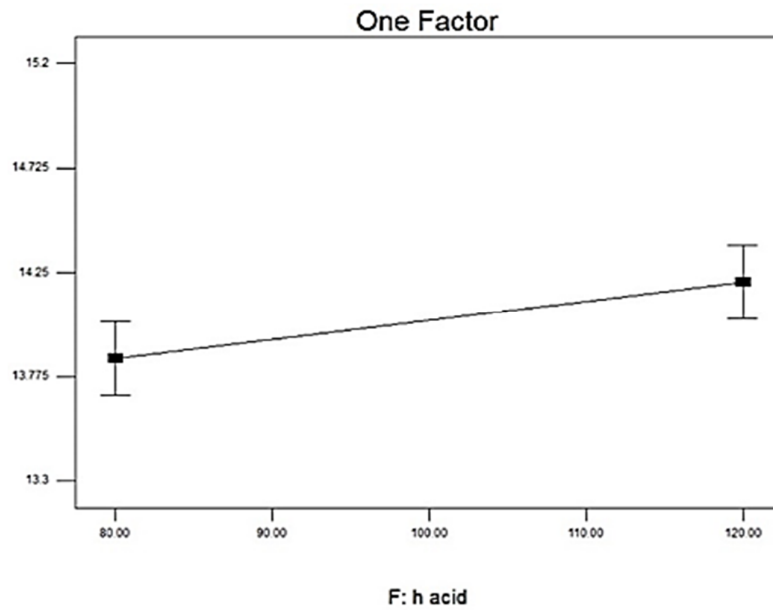


Figure 16. Graphic representation of humic acid concentration (F) on antimony grade.

**6.3. Statistical investigation of flotation tests with the purpose of weight recovery**

According to Figure 17, by selecting factors E, A, F, AD, AE, BD (collector concentration (A), pH (B), depressant concentration (E), humic acid concentration (F), interaction between collector concentration and the activator (AD), the interaction between the concentration of the collector and the depressant (AE), the interaction

between the pH and the concentration of the activator (BD)) which have the highest effect values, the influence of these factors is scattered and far from the fitting line of the error distribution and compared to other effects, they are concentrated very close to the fitting line. As a result of the initial estimation, it is concluded that the factors E, E, A, F, AD, AE, BD are obvious factors.

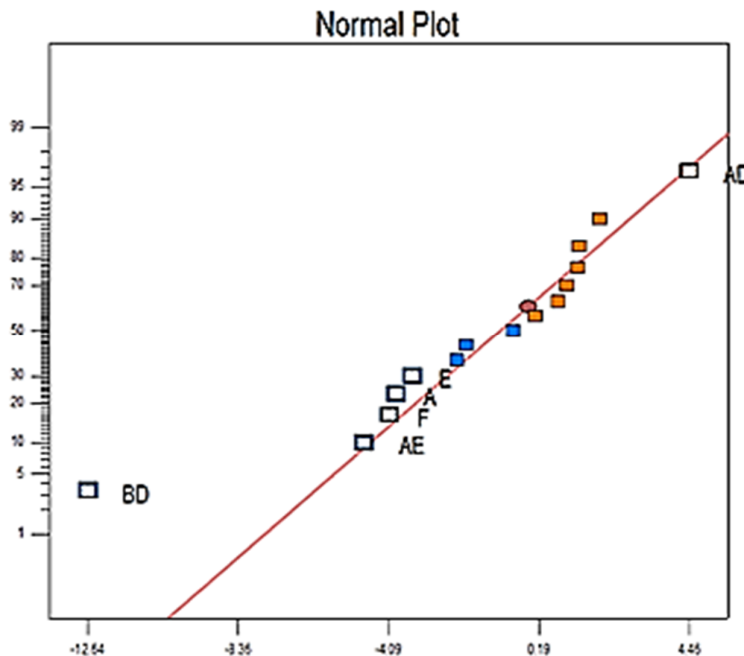


Figure 17. Normal probability curve to check weight recovery of concentrate.

According to Figure 18, by choosing the points E, A, F, AD, AE, BD, the line related to the error distribution is closer to zero, thus it can be said that

the factors E, A, F, AD, AE, BD have a significant effect on antimony recovery concentrates.

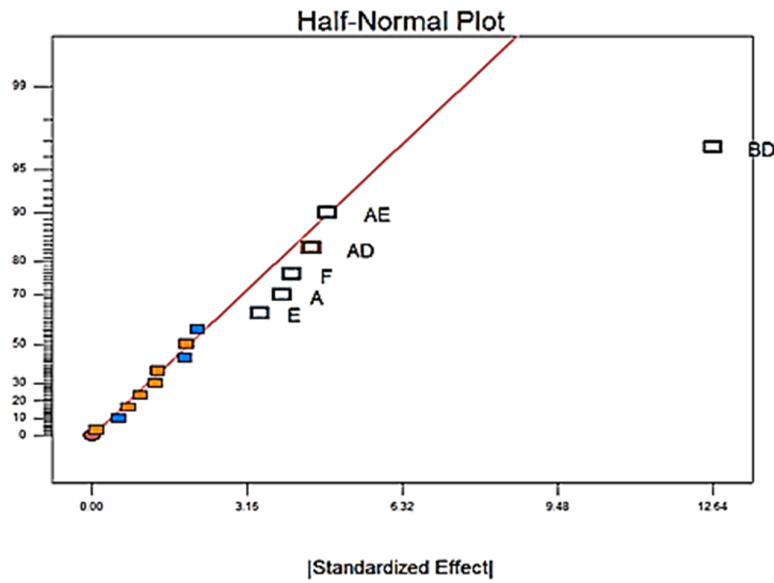


Figure 18. Half-normal probability curve to check weight recovery of concentrate.

According to Figure 19, BD is the most influential parameter on weight recovery of

concentrate, and factors E, A, F, AD, AE, are most likely to influence weight recovery.

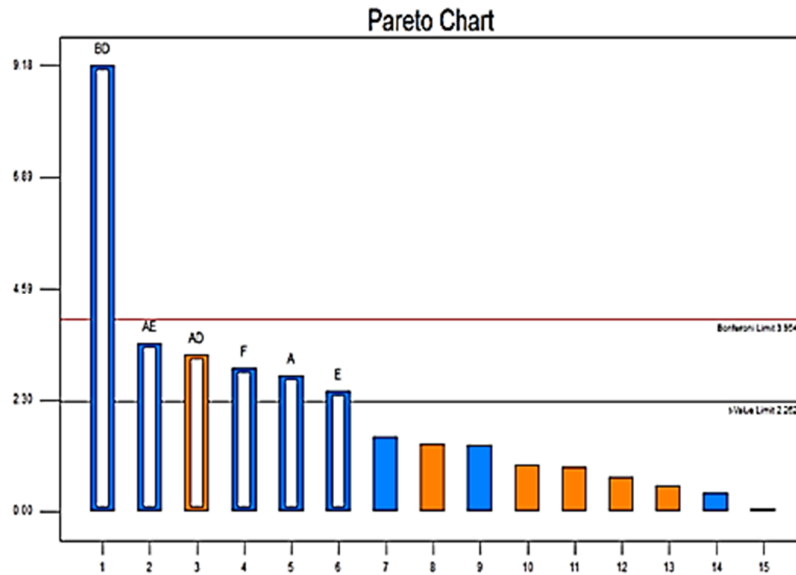


Figure 19. Pareto chart to check weight recovery of concentrate.

In Table 9, the values of the page related to the analysis of variance of the laboratory data and the effect of the factors on the weight recovery of the concentrate are displayed. As can be seen here, the model is significant with high confidence.

Effective factors in the model include E, A, F, AD, AE, BD. In terms of importance and impact, the softening factor has been determined to be the most effective factor on the amount of weight recovery in the concentrate.

**Table 9. Values of the ANOVA page to check the recovery of antimony concentrate.**

agents	sum of squares	Degree of liberation	mean sum of squares	Fisher's value distribution (F value)	significant level (P value)	
model	984.64	8	123.08	13.05	0.0014	significant
Collector concentration (A)	59.68	1	59.68	6.33	0.0401	
pH (B)	2.18	1	2.18	0.23	0.6456	
Activator concentration (D)	0.031	1	0.031	3.248E-003	0.9561	
Depressant concentration (E)	46.58	1	46.58	4.94	0.0616	
Humic acid concentration (F)	66.02	1	66.02	7.00	0.0331	
The interaction between the concentration of the collector and the activator (AD)	79.66	1	79.66	8.45	0.0228	
The interaction between the concentration of the collector and the depressant (AE)	91.68	1	91.68	9.72	0.0169	
The interaction between the concentration of the pH and the activator (BD)	638.83	1	638.83	67.75	0.0001>	
Remains	66.00	7	9.43			

With these interpretations, the considered mathematical model has become meaningful. Other factors did not significantly affect the amount of weight recovery in the concentrate. The

appropriate mathematical model calculated for the calculation of recovery and considering the coding values of the factors is in the form of equation 6.

$$\text{Recovery} = 55.86 - 1.93 * A + 0.37 * B + 0.044 * D - 1.71 * E - 2.03 * F + 2.23 * A * D - 2.39 A * E - 6.32 * B * D \tag{6}$$

Figure 20 shows that the interaction between the concentration of the collector and the activator (AD) has a direct effect on the amount of antimony recovery of the concentrate, by increasing the amount of the collector from 800 to 1200 g/t for antimony recovery when using the activator concentration of 300 g/t decreases and when using the activator concentration of 500 g/t, it increases. An X-ray photoelectron spectroscopy (XPS) study indicated that a film of PbS formed at the stibnite surface after the stibnite was conditioned with a Pb (NO<sub>3</sub>)<sub>2</sub> solution (Qinbo Cao 2018). It is generally believed that the activation effect of Pb<sup>2+</sup> depends on the surface adsorption of Pb<sup>2+</sup> at the stibnite surface [23]. As expected, the substitution of the Pb atom for the Sb atom at the stibnite surface could also occur [24].

Figure 21 shows that the interaction between pH and activator concentration (AD) has an indirect

effect on the antimony recovery value of the concentrate, with the increase in pH from 6 to 8, the antimony recovery when using the activator concentration of 300 g/t increases and when using an activator concentration of 500 g/t is reduced. As known from the literature, the addition of lead nitrate in the flotation of antimony ores improves the flotation conditions at 6.5 pH and more than 89% of the added lead is adsorbed on the antimony ores surface as Pb<sup>2+</sup> ions. Pb<sup>2+</sup> adsorption on the negatively charged antimony ores surface causes an increase in the zeta potential of antimony ores. Studies have shown that this effect depends on the amount of added Pb(NO<sub>3</sub>)<sub>2</sub> and is an optimum value. For this reason, experiments were carried out to determine the optimum amount of Pb Nitrate. Then antimony grade increased in an activator concentration of 300 g/t., but it decreased in an activator concentration of 500 g/t.

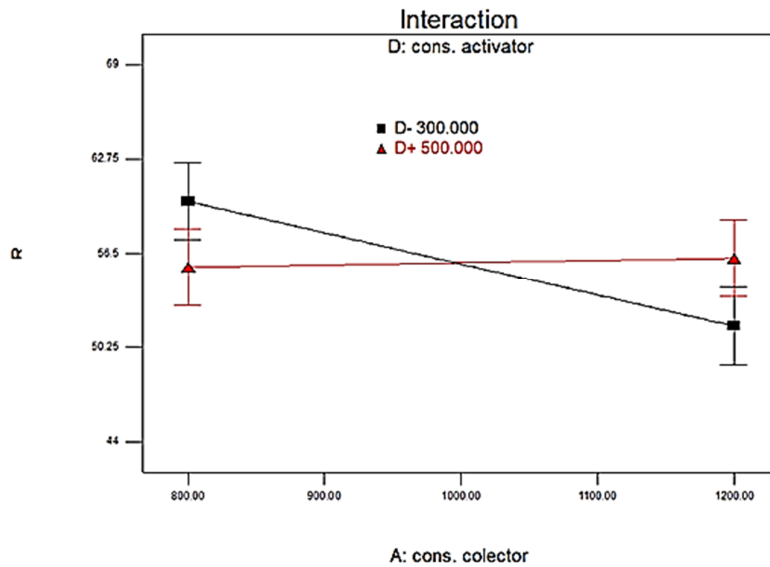


Figure 20. Graphic representation of collector and activator concentration interactions on concentrate weight recovery.

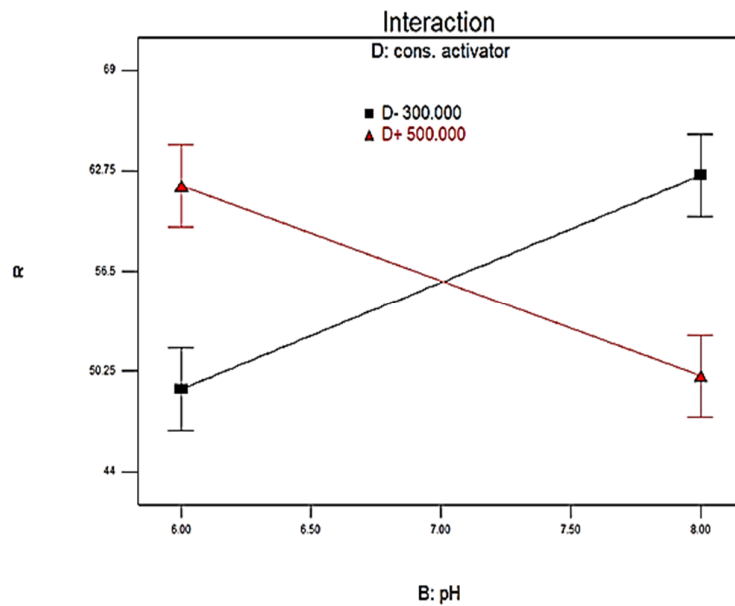


Figure 21. Graphic representation of AD interactions on concentrate weight recovery.

Figure 22 shows that the interaction between the concentration of the collector and the depressant (AE) has an indirect effect on the amount of antimony recovery of the concentrate, with the increase of the collector concentration from 800 to

1200, the recovery of antimony when using the depressant concentration of 2500 g/t, increases and when using the depressant concentration of 4000 g/t, it is reduced.



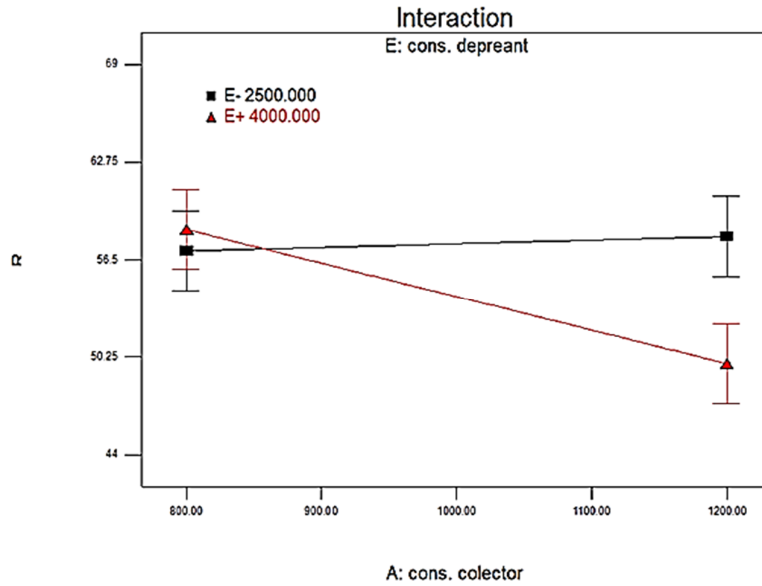


Figure 22. Graphic representation of AE interactions on concentrate weight recovery.

Figure 23 shows that the concentration of humic acid (F) has an indirect effect on the amount of antimony recovery in the concentrate, as the concentration of humic acid increases from 80 to 120, antimony recovery decreases. The humic acid has influences on removal process of aqueous heavy metals. Humic acid tends to be adsorbed on

various mineral colloids, which affects the transport of mineral colloids and the pollutants they adsorbed [20]. It has been reported that a high concentration of humic acid prevents or delays the transition of Fe(III) in a mineral phase with low crystallization [21,22]. Then humic acid was found to inhibit antimony recovery.

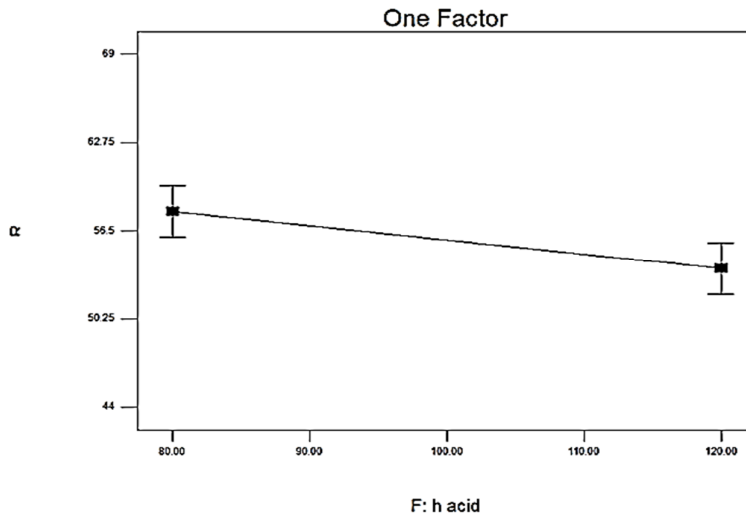


Figure 23. Showing the effect of humic acid on the weight recovery of the concentrate.

7. Conclusions

Antimony ore flotation with a grade of 4.32% was carried out in a two-step method, in which, in the first step, antimony sulfur (stibnite, Sb<sub>2</sub>S<sub>3</sub>) was collected at the pH determined by adding copper

sulfate activator, lead nitrate and depressant. Together, potassium amyl xanthate collector and MIBC frother was added (preparation time for sodium silicate activator and depressant is 3 minutes, collector is 2 minutes and MIBC is 1 minute) and the concentrate is collected for 4.5

minutes and a cleaner step was performed on the collected concentrate for 3 minutes, the it was analyzed after dewatering and drying. In the second stage of flotation, the tailings of the first stage of flotation for antimony oxides was done (the preparation time for the activator is 3 minutes, the collector is 2 minutes and the MIBC is 1 minute) and the concentrate was collected for 4.5 minutes and a cleaner step was performed on the collected concentrate. After collecting the concentrate for 3 minutes, the concentrate was analyzed after dewatering and drying. The results of the tests showed in the optimum conditions: pH 8, Collector concentration 800 (g/t), Activator concentration 300 (g/t), Depressant concentrate 2500 (g/t), Activator type  $Pb^{2+}$  and Humic acid concentration 80 (g/t), 68.99% recovery and 13.32 grade were obtained. With the increase of the collector amount from 800 to 1200 g/t, the antimony grade decreases when using the depressant concentration of 2500 g/t, and increases when the depressant concentration is 4000 g/t. With an increase in pH from 6 to 8 antimony grade decreases when using an activator concentration of 300 g/t, and it decreases when using an activator concentration of 500 g/t. The concentration of humic acid has a direct effect on the antimony grade. The interaction between the concentration of the collector and the activator has a direct effect on the antimony recovery, by increasing the amount of the collector from 800 to 1200 g/t, the recovery of antimony, when using the activator concentration of 300 g/t, decreases and when using the activator concentration it increases by 500 g/t. The interaction between pH and activator concentration has an indirect effect on the amount of antimony recovery, with an increase in pH from 6 to 8, antimony recovery increases when using an activator concentration of 300 g/t, and increases when using an activator concentration of 500 g/t it decreases. The interaction between the concentration of the collector and the depressant has an indirect effect on the amount of antimony recovery of the concentrate, with the increase of the concentration of the collector from 800 to 1200, the recovery of antimony increases when using the concentration of the depressant is 2500 g/t, and it decreases when using the concentration of the depressant is 4000 g/t. The concentration of humic acid has an indirect effect on the amount of antimony recovery in the concentrate, as the concentration of humic acid increases from 80 to 120, antimony recovery decreases.

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## فلوتاسیون کانه اکسیده آنتیموان سفیدابه

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### چکیده:

ماده معدنی اصلی و اقتصادی آنتیموان استینیت یا سولفید آنتیموان می باشد و تحقیقات و فرآیندهای موجود در دنیا براساس آن استوار می باشد و کانی‌های اکسیدی بدلیل دشواری فرآوری و عدم کارایی مطلوب روش فلوتاسیون، جزو ذخایر اقتصادی و دارای اهمیت آنتیموان بشمار نمی روند. از طرفی با توجه به اینکه بخش بزرگی از ذخیره آنتیموان سفیدابه را کانسنگ اکسیده کم عیار تشکیل داده است؛ این پژوهش بر روی روش استحصال اقتصادی و امکان بازیابی این نوع ذخیره با توجه به استراتژیک بودن فلز آنتیموان دارای اهمیت خواهد بود. با توجه به آزمایش‌های انجام شده در این پژوهش، پارامترهای موثر برای فلوتاسیون که شامل: pH، غلظت کلکتور، غلظت فعال کننده، غلظت بازداشت کننده، نوع فعال کننده، غلظت هیومیک اسید، هستند. برای مدلسازی آماری آزمایش‌ها از نرم افزار DX7 استفاده شده است. براساس پارامترهای فوق، طراحی آزمایش به روش فاکتوریل جزئی انجام و در نهایت تعداد ۱۶ آزمایش برای تأثیر عوامل فوق بر عیار و بازیابی وزنی نمونه تعیین شد. فلوتاسیون کانسنگ آنتیموان با عیار ۴/۳۲٪ به روش دو مرحله ای انجام شد که در این روش در مرحله اول ابتدا سولفور آنتیموان (استینیت، Sb<sub>2</sub>S<sub>3</sub>) در pH تعیین شده با اضافه کردن فعال کننده سولفات مس یا نیترات سرب و بازداشت کننده با هم، کلکتور پتاسیم آمیل زنتات و کف ساز MIBC فلوتاسیون انجام شد. در مرحله دوم فلوتاسیون، باطله مرحله اول فلوتاسیون برای اکسیدهای آنتیموان با کلکتور اولئات سدیم (با غلظت های تعیین شده) در pH تعیین شده انجام شد با اضافه کردن فعال کننده سولفات مس یا نیترات سرب، کلکتور اولئات سدیم و هیومیک اسید و کف ساز MIBC فلوتاسیون انجام شد. در بهترین شرایط با فلوتاسیون دو مرحله ای آنتیموان، بازیابی ۶۸/۹۹٪ و عیار ۱۳/۳۲ بدست آمد.

**کلمات کلیدی:** استینیت، کانی اکسیدی آنتیموان، فلوتاسیون، معدن سفیدابه.