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CONCENTRATION OF BARITE AND FLUORITE MINERALS OF
ESKİŞEHİR-BEYLİKAHIR DISTRICT

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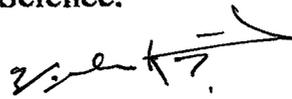
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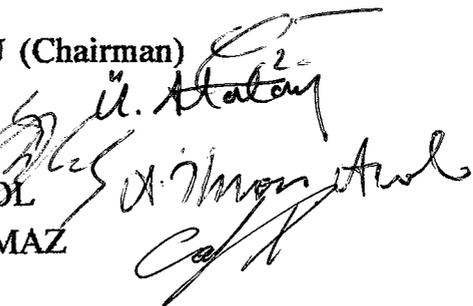
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ABSTRACT

CONCENTRATION OF BARITE AND FLUORITE MINERALS OF ESKİŞEHİR-BEYLİKAHİR DISTRICT

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M.S. in Mining Engineering

Supervisor: Assoc. Prof. Dr. Cahit HİÇYILMAZ

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In this study, concentration possibilities of barite and fluorite minerals of Eskişehir-Beylikahır district were investigated.

Concentration studies were carried out on composite samples obtained by mixing representative samples of Küçükhöyüktepe and Devebağirtantepe in the ratio of 2 to 1.

Mineralogical analyses of the ore indicated that barite, fluorite, bastnasite, calcite, and mica minerals were the major minerals in the composite ore. Chemical analyses showed that composite ore contains 52.47% CaF_2 , 25.40% BaSO_4 , and approximately 6.0% rare earth elements.

During the concentration studies, gravity concentration, flotation, and high intensity magnetic separation were applied to composite ore separately or in combination.

By applying gravity concentration-flotation-magnetic separation combination barite concentrate suitable for chemical

manufacturing, and fluorite concentrate marketable as no.2 ceramic grade were obtained. The highest grades of fluorite and barite concentrates obtained were 92.18% CaF_2 with 45.42% recovery and 94.52% BaSO_4 with 36.91% recovery, respectively.

Key words: Eskişehir-Beylikahır District, Barite and Fluorite Minerals, Gravity Concentration, Flotation, Magnetic Separation.

Science Code: 607.02.03



ÖZ

ESKİŞEHİR-BEYLİKAHIR BÖLGESİ BARİT VE FLUORİT MİNERALLERİNİN ZENGİNLEŞTİRİLMESİ

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Bu çalışmada Eskişehir-Beylikahır bölgesi barit ve fluorit minerallerinin zenginleştirilme olasılıkları araştırılmıştır.

Zenginleştirme çalışmaları, Küçükhöyüktepe ve Devebağirtantepe temsili numunelerinin 2:1 oranında karıştırılmasıyla elde edilen bileşik numuneler ile gerçekleştirilmiştir.

Cevher üzerinde yapılan mineralojik analizler bileşik numunedeki temel minerallerin barit, fluorit, bastnasit, ve mika mineralleri olduğunu göstermiştir. Kimyasal analizlere göre bileşik numune %52.47 CaF_2 , %25.40 BaSO_4 , ve yaklaşık %6 nadir toprak elementleri içermektedir.

Zenginleştirme çalışmaları sırasında, gravite zenginleştirme, flotasyon, ve yüksek alan şiddetli manyetik ayırma, bileşik numuneye ayrı ayrı veya kombinasyon olarak uygulanmıştır.

Gravite zenginleřtirme-flotasyon-manyetik ayırma kombinasyonunun uygulanmasıyla, kimyasal üretime uygun barit konsantresi, ve no.2 seramik tenörlü fluorit konsantresi elde edilmiştir. Elde edilen en yüksek tenörlü konsantreler, %45.42 randımanlı %92.18 CaF₂ içerikli fluorit konsantresi ile %36.91 randımanlı %94.52 BaSO₄ içerikli barit konsantresidir.

Anahtar Kelimeler: Eskişehir-Beylikahır Bölgesi, Barit ve Fluorit Mineralleri, Gravite Zenginleřtirme, Flotasyon, Manyetik Ayırma.

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CHAPTER I

INTRODUCTION

Eskişehir-Beylikahır complex ore body is one of the biggest known deposit in Turkey, not only in thorium content but also in rare earth elements content. On the other hand, barite and fluorite reserves of the ore body are also great. Totally, barite and fluorite reserve of the Eskişehir-Beylikahır area is more than 20,000,000 tons (Erseçen, 1989).

Barite is a heavy, soft, and chemically inert mineral that contains 58.8% barium (Ba) and 41.2% sulphate (SO₄). It is also known as barytes, heavy spar, tiff, and cawk. Barite has a specific gravity of 4.5. Specifications for barite vary according to its different uses. Material for weighting muds must be finely ground, heavy and chemically inert; consequently, barite for this purpose must have a specific gravity of 4.2 or higher, and 90% to 95% of the material must pass a 325 mesh (44 µm) screen. The grade of barite for weighting muds changes from 83-90% BaSO₄ to 90-95% BaSO₄, according to O.C.M.A. (Oil Companies Material Association-London) and A.P.I. (American Petroleum Institute) respectively. In chemical manufacturing minimum 94% BaSO₄ grade is required. Glass manufacturers usually require a minimum of 95% BaSO₄ (Morse, 1980a).

Mineral fluorspar (CaF₂), or fluorite is the most important resource of fluorine which is a pale-yellow, corrosive gas. It is a fairly heavy mineral with a hardness of 4 on the Mohs scale and a specific gravity ranging from 3.01 to 3.60. In crystalline form fluorite exhibits a wide range of colors, from

colorless to yellow, blue, purple, green, rose, red, bluish and purplish black, and brown. Three principal grades of fluorspar are available commercially- acid, ceramic and metallurgical. Acid-grade fluorspar (acid-spar) contains at least 97% CaF_2 . Ceramic-grade fluorspar (ceramic-spar) is generally marketed as No. 1 ceramic, containing 95% to 97% CaF_2 , and No. 2 ceramic, containing 85% to 93% CaF_2 . Metallurgical-grade fluorspar (met-spar) contains about 60% to 85% CaF_2 . In the United States of America, met-spar is usually quoted in terms of effective CaF_2 units, obtained by subtracting 2.5 times the silica content of the ore from its total CaF_2 content (Morse, 1980b).

Beneficiation methods of barite and fluorite minerals are gravity concentration, and flotation. Eskişehir-Beylikahır complex barite-fluorite-bastnasite ore deposit due to its complex structure, can be operated for the production of one or more elements and/or minerals. The purpose of this study was to investigate the concentration possibilities of barite and fluorite minerals from the Beylikahır complex ore, and to find simple and inexpensive concentration flowsheets for different uses of barite and fluorite minerals in industry.

CHAPTER II

BEYLİKAHIR COMPLEX BARITE AND FLUORITE ORE DEPOSIT

2.1 General Information

Beylikahır complex barite and fluorite ore deposit which also containing rare earth minerals is situated near Sivrihisar county of Eskişehir city. Mihallıçcık county and Sivrihisar county are located to the Northeast and Southeast of the ore deposit respectively. Beylikahır and Kaymaz subdistricts are located to the Northwest and Southwest of the ore deposit respectively (Figure 1).

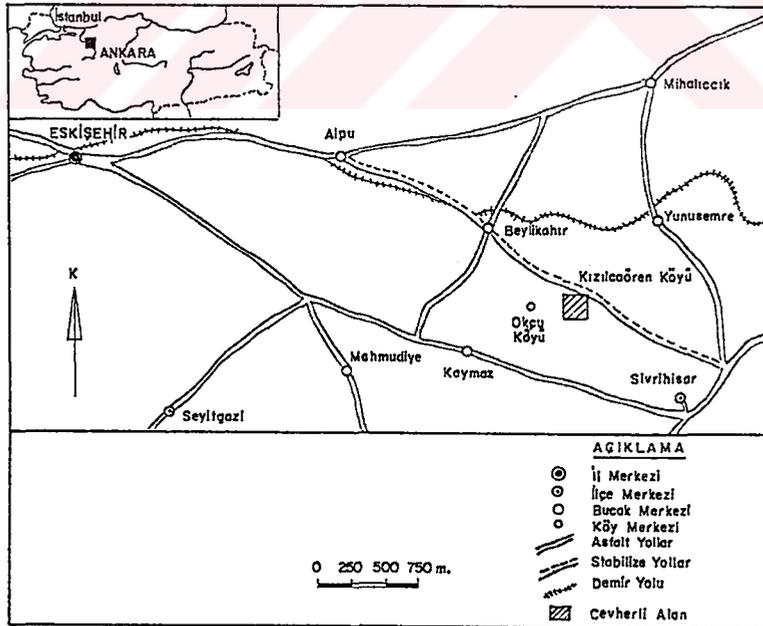


Figure 1. Location of the Eskişehir-Beylikahır District

2.2 Geology

The geological research on the Eskişehir- Sivrihisar-Beylikahır area has been studied since 1959 by M.T.A. It was estimated from the data obtained that the deposit type is hydrothermal. Serpentinites probably the oldest rock type of the area are located to the South of the Kızılcaören-Küçükhöyüktepe complex ore body.

Serpentinites close to the surface or tectonic lines have a siliceous appearance, due to the silicification. Also, at the same zones, limonites are observed.

Meta greywacke, siltstone, diabase and tuff which are the units creating the wallrock of the ore body, are placed over the serpentinites and siliceous serpentinites (Çiftçi and Kumru, 1985).

2.3 Ore Minerals

The genesis of the complex ore (fluorite- barite- rare earth minerals) located in the weak zones of the wallrock as veins, is related to dioritic and syeritic rocks.

Pneumatolytic and hydrothermal solutions concerning ore mineralization have released metal containing minerals in deep seated zones. After the volcanisms, the solutions free from metallic ions and rich in Ca^{2+} , F^- , Ba^{2+} and SO_4^{2-} ions have intruded into the fissures of the wallrock which made up of meta greywacke, siltstone, diabase and tuff created by tectonisms. The existence of the ore in this units is sometimes as layers, bands and lenses, but generally as veins.

Thin section studies made by M.T.A. showed that, fluorite particles contained partially crypto and micro barites,

and barite particles contained partially crypto and micro fluorites. Therefore, it can be estimated that barite and fluorite minerals were formed at the same time. In addition, both barite and fluorite minerals contained rare earth mineral or minerals as micro and crypto forms. Also, the existence of pure fluorite mineral was found during these studies.

Pyrite which can be found as opaque mineral in the Eskişehir-Sivrihisar-Küçükhöyüktepe complex barite-fluorite ore, has turned into limonite as a result of alteration. Manganese minerals are mostly psilomelane and rarely pyrolusite. Mineralogical determinations showed that not only hematite, but also magnetite could be found in the reserve area in very small amounts. Bastnasite [(Ce, La, Nd) FCO_3] is the most widely seen rare earth mineral in the vein fillings. Rarely brockite [(Ca, Th, Re, (PO_4)) H_2O] is found also (Kaplan, 1977). In the ore all of these minerals can be found at the same place, but sometimes one or several of them can be lesser or more (Çiftci and Kumru, 1985).

During the mineralogical and X-ray studies made on different samples, no independent thorium mineral was found. Thorium is contained in bastnasite and brockite minerals (Kaplan, 1977).

2.4 Reserve

Detailed geological studies on Eskişehir- Sivrihisar- Beylikahır complex ore body made by Industrial Raw Materials Department of M.T.A., showed that, ore body has 11,300,000 tons (proved+ probable reserve) of fluorite assaying 37.44% CaF_2 , and 9,400,000 tons (proved+ probable reserve) of barite assaying 31.00% BaSO_4 (Erseçen, 1989).

Also, it was proved that 1,278,949 tons (proved reserve) of rare earth elements assaying 3.52% (La+ Ce+ Nd) and 380,000 tons of thorium assaying 0.2% ThO₂ exist in the ore body (Çiftçi, 1986).

Devebağirtantepe, Küçükhöyüktepe, Yaylabaşı, Köyveri, Kocayayla, Kocadevebağirtan, Canavarini Sırtı are the names of the sectors in which the complex ore body exists. The average specific gravity of the complex ore is 3.64 (Çiftçi and Kumru, 1985).

CHAPTER III

PREVIOUS STUDIES ABOUT CONCENTRATION OF BARITE AND FLUORITE MINERALS

3.1 Gravity Concentration of Barite and Fluorite Minerals

3.1.1 Shaking Table Concentration

Zadra et al. (1952) used laboratory Wilfley shaking table to separate bastnasite and barite minerals of Mountain Pass bastnasite ore (California, U.S.A.). But, an incomplete separation of bastnasite and barite resulted. As the specific gravity of bastnasite is near that of barite, the interlocked minerals were, therefore, of nearly the same gravity and could not be separated by gravity concentration, but considerable gangue containing little of either mineral could be discarded after liberation by grinding. Also, laboratory Wilfley shaking table was used by Zadra et al. (1952), in order to separate the cerium mineral in fluorspar ores from Zuni Milling Co. (Albuquerque-New Mexico, U.S.A.). The cerium mineral was corresponded in rare-earth content to bastnasite and was probably of that type. Run of mine ore contained 41% CaF_2 , 10% BaSO_4 , about 0.5% CeO_2 , and 0.7% other rare-earths. Flotation concentrates were fed to shaking table. Two concentrates and a tailing were produced during tabling operation. The first concentrate contained 5.3% CeO_2 , 6.6% other rare earths, 45.5% CaF_2 , and 37.6% BaSO_4 , representing 67% of the rare earths, 8% of the fluorspar, and 34% of the barite in the flotation concentrates. The second table concentrate contained 84.3% CaF_2 , 8.8% BaSO_4 , and only 0.1% CeO_2 , and 0.1% other rare

earths. Recoveries were 49.5% of the fluorspar, 25.5% of the barite, 4.1% of the CeO_2 , and 3.0% of the other rare earths in the flotation concentrates. This product was marketable as metallurgical fluorspar.

Gençtan (1967) worked on the concentration problems of low-grade fluorspar ore of Kaman-Şefaathlı district, assaying 22.89% CaF_2 , 18.94% SiO_2 , and 56.66% CaCO_3 . During the studies, metallurgical grade fluorite concentrate assaying 71.98% CaF_2 with 58.58% recovery was produced by using laboratory Wilfley shaking table.

Sivrihisar-Beylikahır-Eskişehir complex ore was tried to be concentrated by Kutluata and Özden (1985). For this purpose, samples of different size fractions were concentrated by shaking table and a fluorite concentrate assaying 63.53% CaF_2 was obtained with 64.52% recovery.

Çiftçi (1986) was also used shaking table during his studies performed on samples collected from Sivrihisar-Beylikahır-Eskişehir complex ore. The sample contained on average 48.5% CaF_2 , 28.50% BaSO_4 , and 7.70% rare earth elements. From this ore, barite pre-concentrate and fluorite pre-concentrate were recovered. Grade and recovery of barite pre-concentrate were 85.98% BaSO_4 and 43.75% respectively. Grade and recovery of fluorite pre-concentrate were 64.92% CaF_2 and 72.16% respectively. Barite pre-concentrate was upgraded after grinding by applying high intensity magnetic separation followed by shaking table concentration. Barite final concentrate had 91.92% BaSO_4 grade with 41.74% recovery.

Shaking table was used for the concentration studies of fluorite and barite from Beylikahır-Eskişehir complex ore containing on the average 34.7% CaF_2 , 32.2% BaSO_4 , 2.70% rare earth elements and 0.11% ThO_2 , by Yüce et al., (1992). Shaking table tests were carried out for minus 0.3 mm sample. A barite

concentrate assaying 85.5% BaSO₄ with 55.8% recovery, and a fluorite pre-concentrate assaying 63.2% CaF₂ with 64.1% recovery were obtained.

3.1.2 Jigging

The upgrading process at the Barega barite mine (Sardinia) consists of two jigging stages in series. In the first stage, the entire feed range (-20 mm) is treated in two parallel oscillating frame jigs, each having a throughput capacity of 45 t/h. The final cleaning stage is carried out in four fixed frame jigs, each having a capacity of 7-8 t/h (Carbini et al., 1987).

3.2 Flotation Concentration of Barite and Fluorite Minerals

3.2.1 Flotation Concentration of Barite

Barite is readily floated with oleic acid, fatty acid sulphonates, and sodium taurate in the alkaline and neutral pH range, and is easily depressed in a circuit made acid with sulphuric acid. Sodium silicate is frequently used in these systems for the depression of quartz. As the flotation response of fluorite and calcite is somewhat similar, with fatty acids as collectors, the separation from these minerals has presented difficulties (Davis, 1985).

Zadra et al. (1952), used flotation to separate barite from bastnasite ore of Mountain Pass (California, U.S.A.). The ore was ground to minus 65 mesh (-208 µm) and in later tests to minus 100 mesh (-147 µm). Oleic acid was used as collector reagent with a very large variety of conditioning reagents and frothers. Separation of barite from bastnasite was poor because of the intimate locking of the mineral grains. Concentrates containing as high as 85% BaSO₄ were produced, but recovery

of barite was low. At the other extreme, tailings with as low as 5% barite were made when concentrate grade was poorest. It was reported by Zadra et al. that various dispersant reagents and desliming before flotation have been tried with no improvement in results. Barite flotation was also applied to fluorspar ores of Zuni Milling Co. (Albuquerque-New Mexico, U.S.A.) which containing cerium minerals. The barite was more friable than either the fluorspar or the cerium mineral and more of the barite was slimed, which was a slight advantage since only a little separation in flotation was possible in the rougher-concentration stage. The ore was ground to minus 100 mesh (-147 μm) in several stages to avoid sliming. Oleic acid was used as collector. The concentrates after one cleaning stage carried 72% CaF_2 , 15% BaSO_4 , 1.1% CeO_2 , and 1.4% other rare earths. Recoveries were about 90% of the rare earths and 80% of fluorspar.

The U.S. Bureau of Mines studied the potential for recovering marketable barite concentrates that meet oil-well drilling-mud specifications from barite waste pond materials. Flotation tests were conducted using several types of barite waste materials with widely varying character, size, and barite content. These tests have shown that high-grade concentrates that meet oil well drilling-mud specifications can be produced from these widely divergent materials with high recovery of the barite. The waste materials had head analyses ranging from 3.1 to 68.7% BaSO_4 . Flotation using sodium silicate and sodium cetyl-stearyl sulphate produced cleaned concentrates with BaSO_4 contents ranging from 95.0 to 96.9%. The amount of barite reporting to the cleaned concentrates ranged from 81.2 to 95.9% of the barite in the feed (Lamont and Sullivan, 1982).

Bolin (1983) studied the barite flotation by using sulphonate and alkyl sulphate reagents and found a difference between these reagents. He showed, fast, efficient flotation of barite particles when alkyl sulphate reagents were added.

Alkyl sulphates caused the barite particles to flocculate and give a faster flotation, about two minutes compared to six for the sulphonate reagent. He found also that, the alkyl sulphates gave after only two cleaner stages not only better selectivity but also a high grade more than 95% BaSO₄. But the sulphonate reagent gave less than 80% BaSO₄ in the concentrate.

Houot et al. (1985) studied the flotation of barite with industrial collectors of the sulphonate type that were currently used in the Chaillac plant (Indre, France). Samples of pure barite from Chaillac ore were floated, and optimum results were obtained when pH was 8-9. Also, it was concluded that the water quality was very important parameter in barite flotation. For example, the Ca²⁺ ions react with the sulphonate at a very low concentration (5×10^{-6} mole/l), and SO₄²⁻ ions depress the barite. The other ions that were investigated have a weak influence (HCO₃⁻, Cl⁻), which may be mildly beneficial (CO₃²⁻). No flocculation was observed during conditioning with the sulphonate reagents, but it was observed from the beginning of pulp aeration.

De Cuyper and Broekaert (1986) developed a flowsheet to produce barite concentrates for oil-well drilling mud uses and fluorspar concentrates of acid-grade quality from complex ores containing barite and fluorspar, using reagents less sensitive to water hardness. In this flowsheet, firstly, bulk flotation of sulphide minerals was carried out at pH 8.5 with sodium diisopropyl dithiophosphate and copper sulfate. Secondly, celestobarite was floated selectively at pH 9 with alkyl-sulfate as collector, barium chloride and citric acid as modifying agents. And finally, selective flotation of fluorspar was applied with alkyl-sulfonate as collector, and starch as depressant, at pH 6.5-7.0.

Sodium silicate and lignin sulphonate were used as depressants for fluorite, bastnasite, quartz and oxides, for the

flotation of barite from barite-fluorite complex ores containing bastnasite. As a collector for barite, sodium alkyl sulphate emulsified with petroleum was used (Merker et al., 1991).

3.2.2 Flotation Concentration of Fluorite

The commercially floated ore, fluorite, occurs in association with silica, calcite, barite and sometimes such sulphides as lead, zinc or iron. These last are floated or removed by gravity concentration before dealing with the fluorite. The market for acid-grade CaF_2 demands a high degree of purity, and the treatment usually calls for thorough recleaning to remove the last of the calcite and silica. The conventional reagent plan controls pH by the use of soda-ash or sodium hydroxide. The depressants for gangue minerals notably calcite, are quebracho (a tannin extract from the bark of a tree of the name), dextrin and sodium silicate. The collector agent is oleic acid or one of its modifications. Sodium silicate is used as a dispersant in fluorite flotation. Potassium dichromate may be used to depress any sulphides not previously removed by sulphhydryl collectors (Pryor, 1979).

Gençtan (1967) was made flotation tests on low-grade fluorspar ore of Kaman-Şefaatlı district, assaying 22.89% CaF_2 , 18.94% SiO_2 , and 56.66% CaCO_3 , and obtained a fluorite concentrate assaying 94.52% CaF_2 with 56.35% recovery by using quebracho, depressant 65 (reagent of Float Ore company) to depress quartz and iron oxides, and R-411 (partially distilled tall oil; a selective collector for fluorite including oleic acid and linoleic acid). Selective flotation of fluorite-calcite mixture was studied by Tolun et al. (1973). For this purpose, Tolun et al. studied the flotation characteristics of synthetically prepared fluorite-calcite samples, and showed that, it was possible to float fluorite by the use of an oleic acid based collector at pH 9, under the depressing effect of Na_2SiO_3 and starch.

Oleoylsarcosine was used instead of oleic acid as collector in the flotation of fluorite from ores containing higher calcite contents (Schubert and Baldauf,1990).

Quebracho is a well known depressant used in the selective flotation of fluorite from fluorite-calcite mixtures. The adsorption of oleate and quebracho on both fluorite and calcite is competitive, i.e. either compound decreases the adsorption of the other. The decrease in the adsorption of oleate due to quebracho is, however much stronger for calcite than for fluorite. This is presumably due to a stronger adsorption of oleate on the fluorite (Iskra et al.,1973). Quebracho depresses the flotation of fluorite in a wide range of pH (above 7 and below 5.5), except for a narrow range \approx pH 6. In the presence of calcium ions quebracho completely depresses the flotation of fluorite over the whole pH range, whereas, in the absence of quebracho, the Ca^{2+} ions do not depress the flotation of fluorite (Iskra and Kielkowska, 1980). Bekiřođlu (1973) proved that ordinary corn starch can be used instead of old reagents such as quebracho. It was shown that, acid grade fluorite can be produced by using corn starch which eliminates heating of flotation pulp and the use of quebracho to provide selectivity during the fluorite flotation.

Pugh and Stenius (1985) examined the variations in flotation response for fluorite, as well as apatite and calcite with sodium oleate collector. It was reported that the maximum flotation recovery of apatite and fluorite occurred at about the intermediate pH range with relatively low concentrations of sodium oleate (2×10^{-5} M for fluorite and 7×10^{-5} M for apatite), whereas the flotation of calcite increased with increase in pH and higher concentrations of sodium oleate were required to obtain the same approximate flotation response (3×10^{-4} M). The flotation response for calcite with sodium oleate collector at pH values below 8 was found relatively low.

Fluorite and barite often occur together in nature, and their separation by use of flotation techniques is difficult. Collectors used for one mineral generally float the other also, and it is only by the employment of suitable depressants that any selectivity is obtained. The collectors used fall into the oxyhydril anionic class and include carboxylates, acid alkyl sulphates and sulphonates (Shergold, 1972). De Cuyper and Broekaert (1986) studied the application of direct fluorspar flotation method to the complex fluorspar-celestobarite ores using oleine, potassium dichromate, starch and sodium fluoride. Results showed some difficulties due to great sensitivity of fluorspar flotation to water hardness and to the lack of selectivity of oleine collector towards calcite and celestobarite.

The sodium fluoride-lignin sulphonate process provides a flotation method applicable to a variety of ores, of different grades and mineral association, for recovery of fluorspar from associated gangue materials. The sodium fluoride-lignin sulphonate method is more effective in lowering the silica content in the final product than the quebracho method. Therefore, the effective fluorspar in the metallurgical-grade concentrate would need less fluorspar in the product to obtain the same grade (Eddy et al., 1967). United States Bureau of Mines has developed a flotation process in which lignin sulphonate and sodium fluoride are used for depression of barite, calcite, and silica. Fluorspar is floated with a fatty acid collector. Calcium lignin sulphonate is used for depression of calcite, sodium fluoride was added as a dispersant, oleic acid in an aqueous emulsion is used as a collector for fluorspar, and sodium carbonate is added to lower the solubility of gangue carbonates (Rule and Blake, 1974).

After the barite floated from the barite-fluorite complex ores containing bastnasite, fatty acids are used as fluorite collector. Sodium silicate, lignin sulphonates and sodium fluorosilicate are the depressants for bastnasite and

gangue minerals (Merker et al., 1991). Lignin sulphonates and sodium fluorosilicate are used to depress barite, calcite, and silica during the flotation of fluorite in the flotation mill at Mountain Pass (California, U.S.A.) (Morrice and Wong, 1982).

Çiftçi (1986) has obtained the best results with the stage addition of sodium oleate as collector for fluorite during the flotation of shaking table fluorite pre-concentrate of Sivrihisar-Beylikahır-Eskişehir complex ore.



CHAPTER IV

MATERIALS, METHODS AND EQUIPMENT

4.1 Materials

1177 kg and 1086 kg representative samples were taken from Devebağirtantepe and Küçükhöyüklütepe respectively. Chemical and physical analyses were performed for the characterization of the complex ore.

4.1.1 Chemical Analyses

Not only optic spectrographic semi-qualitative analysis but also mineralogical analysis showed that Devebağirtantepe and Küçükhöyüklütepe samples were very similar to each other (O.D.T.Ü., 1993). Since the reserve of Küçükhöyüklütepe is nearly double of the reserve of Devebağirtantepe, composite sample was prepared by mixing the Küçükhöyüklütepe and Devebağirtantepe samples in the ratio of 2:1.

The results of the chemical analyses of the composite sample are shown in Table 1. 78% of the composite ore is consisted of fluorite and barite, and approximately 6% of it, is rare earth minerals. Calcite and quartz contents of the composite ore is small, totally 4.1%.

Table 1. The Results of the Chemical Analyses of the Composite Sample (O.D.T.Ü., 1993)

Element or compound	Amount by weight	Method of analyses
total rare earth elements	6.5%	ICP
CaCO ₃	2.80%	Gravimetric
SiO ₂	1.30%	Gravimetric
CaF ₂	52.47%	Gravimetric
BaSO ₄	25.40%	Gravimetric
Al ₂ O ₃	4.00%	Gravimetric
Fe ₂ O ₃	3.00%	AAS

4.1.2 Mineralogical Analyses

XRD and mineralogical analyses were performed on the representative samples and hand specimens of Devebağirtantepe and Küçükhöyüklütepe.

XRD analyses of Devebağirtantepe sample showed that it was consisted of fluorite, barite, bastnasite and a small amount of mica minerals. Also, XRD analyses of Küçükhöyüklütepe sample showed that, it was consisted of fluorite, barite and bastnasite minerals.

According to the mineralogical analyses made on hand specimen of Devebağirtantepe, it contained; slightly purple colored fluorite with zone structure and 35-3000 µm particle size (common particle size was 600-800 µm which consisted of 50% of the specimen), barite with particle size of 35-480 µm (common particle size was 60-80 µm which consisted of 35% of the specimen), sub-microscopic material (bastnasite), and very small amount of mica, apatite, opaque minerals.

According to the mineralogical analyses made on Küçükhöyüktepe hand specimen, it contains; darker colored fluorite than Devebağirtantepe with 30-2000 μm particle size (common particle size was 300-500 μm which consisted of 35% of the specimen), barite with 40-1200 μm particle size (common particle size was 200-400 μm which consisted of 25% of the specimen), sub-microscopic material (bastnasite), and very small amount of mica and opaque minerals.

Opaque minerals in the both samples are the same. These are small amount of manganese minerals (polianite, pyrolusite, psilomelane), hematite, pyrite and limonite. Particle size of manganese minerals is 30-40 μm . Pyrite has turned partly or completely into limonite.

4.1.3 Screen Analysis of Composite Sample and Mineral Distributions in Screen Fractions

Wet screen analysis of -8 mesh (2362 μm) size composite ore is given in Table 2. Barite, fluorite, and calcite distributions are given in Table 3.

Fluorite content of the ore is generally found in coarse size fractions. -8 +65 mesh (-2362 +208 μm) fraction which consists of 51.11% of the ore, has 65.13% average CaF_2 grade and contains 63.44% of the total CaF_2 content. But, barite content of the ore is mostly found in finer size fractions. -65 +400 (-208 +37 μm) and -400 mesh (-37 μm) fractions which consist 48.89% of the ore, have 34.45% average BaSO_4 grade and contain 61.87% of the total BaSO_4 content. From the results of wet screen analyses, it can be seen that, 19.18% of -8 mesh (2362 μm) composite ore is below 400 mesh (37 μm) size. Rare earth elements in the ore are also concentrated towards finer screen fractions. Although average Ce and La grades of the ore are 3.00% and 2.70% respectively, in -37 μm fraction Ce and La

grades increase up to 6.40% and 6.20% respectively (O.D.T.Ü., 1993).

Table 2. The Results of Wet Screen Analyses of the Composite Sample

Screen fraction (mesh)	Screen fraction (micron)	weight (%)	Screen oversize (cum. wt. %)	Screen undersize (cum. wt. %)
-8 +10	-2362 +1651	1.09	1.09	98.91
-10 +14	-1651 +1168	7.47	8.56	91.44
-14 +20	-1168 +833	10.34	18.90	81.10
-20 +28	-833 +589	9.86	28.76	71.24
-28 +35	-589 +417	8.25	37.01	62.99
-35 +48	-417 +295	6.41	43.42	56.58
-48 +65	-295 +208	7.69	51.11	48.89
-65 +100	-208 +147	7.12	58.23	41.77
-100 +150	-147 +104	5.99	64.22	35.78
-150 +200	-104 +74	6.53	70.75	29.25
-200 +270	-74 +52	6.29	77.04	22.96
-270 +400	-52 +37	3.78	80.82	19.18
-400	-37	19.18	-	-
Total		100.00		

Table 3. Mineral Distributions of Composite Sample in Screen Fractions

Screen fraction (mesh)	Screen fraction (micron)	wt. (%)	Barite		Fluorite		Calcite	
			BaSO ₄ (%)	dist. (%)	CaF ₂ (%)	dist. (%)	CaCO ₃ (%)	dist. (%)
-8 +28	-2362 +589	28.76	17.78	18.77	68.20	37.37	2.55	20.62
-28 +65	-589 +208	22.36	23.59	19.36	61.20	26.07	2.25	14.13
-65 +200	-208 +74	19.63	41.72	30.09	38.10	14.26	3.30	18.36
-200 +400	-74 +37	10.07	50.03	18.52	32.00	6.14	3.50	9.89
-400	-37	19.18	18.83	13.26	44.20	16.16	6.85	37.00

4.2 Methods and Equipment

4.2.1 Gravity Concentration Equipment

Denver mineral jig and Deister shaking table were the gravity concentration equipment used for barite-fluorite concentration studies of Beylikahır composite ore.

Denver mineral jig has one compartment of 10 x 15 cm sizes, and a jig screen with 2 mm aperture size onto which iron shots are put as ragging material.

Deister shaking table has a diagonal deck riffle pattern. The length of the deck is 128 cm, and the width of the deck is 64 cm. The stroke of the Deister shaking table used was 1 cm. In Deister tables the thin riffles are replaced by other larger riffles at varying intervals which provide pools to permit the settlement of fine grains. In addition, it can also prevent the heavy particles or middlings reporting to the light side.

4.2.2 Flotation Equipment and Reagents

Flotation concentration studies were carried out by using Denver Sub-A laboratory flotation machine with 2 liter fiberglass cell. The speed of the impeller during the flotation tests was fixed at 1200 rpm. Flotation tests were performed with a pulp density of 15% solids by weight. Reagents used during flotation tests are explained in Appendix.

4.2.3 Magnetic Separation Equipment

Magnetic separation tests were performed by using Carpcó model M127 high intensity induced roll magnetic

separator. A specially designed circuit, utilizing a variable voltage transformer and silicon rectifiers, supplies the direct current to energize the field of the magnet. This field is continuously variable from 0 to 12,000 gauss in the operating gap or zone. Rotor speed of the equipment is also continuously variable from 0 to 500 rpm.



CHAPTER V

EXPERIMENTAL RESULTS AND DISCUSSION OF CONCENTRATION STUDIES

5.1 Gravity Concentration Studies

Specific gravities of barite and fluorite minerals are 4.5 g/cm³ and 3.18 g/cm³ respectively. Although the difference between the specific gravities of these minerals is not too much, concentration criterion which is 1.61 shows that the gravity separation of these minerals is possible, but difficult.

$$\text{Concentration Criterion} = \frac{\rho_H \rho_M}{\rho_L \rho_M}$$

where ρ_H is specific gravity of heavy mineral, ρ_L is specific gravity of light mineral, and ρ_M is specific gravity of fluid medium.

5.1.1 Gravity Concentration of Composite Ore Ground to -48 mesh (-295 micron)

In the first gravity concentration test, -8 mesh (2362 μm) composite ore was ground to -48 mesh (-295 μm) with close control to reduce slime. Slime was removed by means of hydrocyclone from the ground ore, since slime would not be

separated efficiently by gravity methods due to their extremely slow settling rates. Fluorite and barite minerals in the ground ore was concentrated by following the flowsheet given in Figure 2.

At the end of this test, a drilling mud grade barite concentrate having 83.45% BaSO_4 with 39.33% recovery was produced. Fluorite concentrate has 61.96% CaF_2 with 87.40% recovery.

In the second shaking table test, to reduce the barite and fluorite losses in slime, it was decided to separate the slime before grinding of the composite ore to -48 mesh (-295 μm) (Figure 3). The grade and recovery of the barite concentrate produced was 85.92% BaSO_4 and 46.82% respectively, while the grade and recovery of the fluorite concentrate produced was 61.98% CaF_2 and 92.49% respectively. Barite concentrate was marketable as drilling mud.

Separation of the slime before grinding was reduced the recovery losses of barite from 4.80% to 1.98%, and fluorite from 9.64% to 4.99%. This process not only increased the grade of the barite concentrate but also increased the recoveries of both barite and fluorite concentrates.

5.1.2 Gravity Concentration of Composite Ore Ground to -65 mesh (-208 micron)

Slime was removed firstly by means of hydrocyclone before grinding of the composite ore to -65 mesh (-208 micron) in this test (Figure 4). Deslimed ore was ground to -65 mesh (-208 micron) with close control. The results of this shaking table test was similar to the results given in Figure 3. Barite concentrate of 84.08% BaSO_4 with 50.15% recovery, and

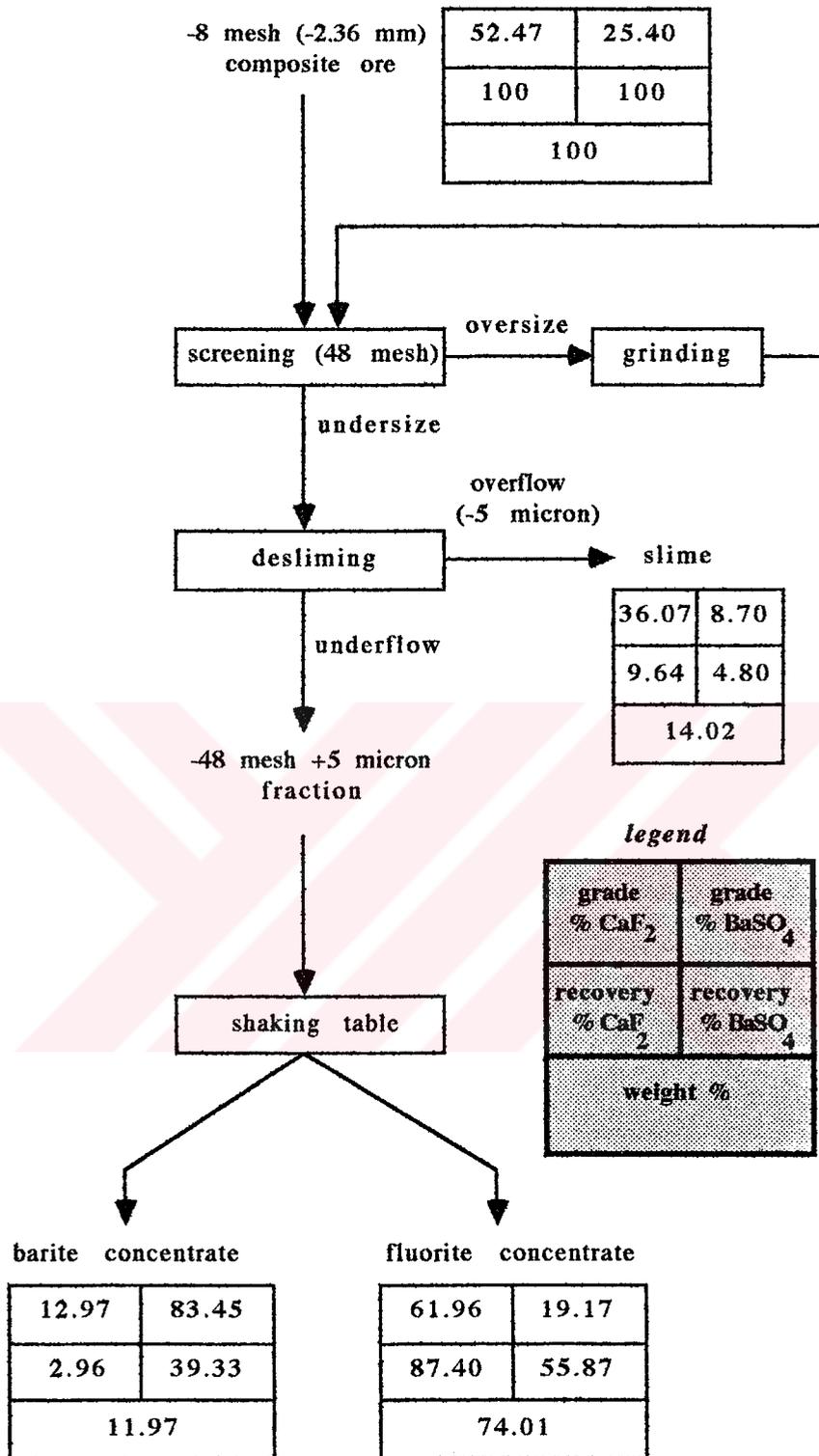


Figure 2. Gravity Concentration of deslimed -48 mesh (-295 μm) Composite Ore

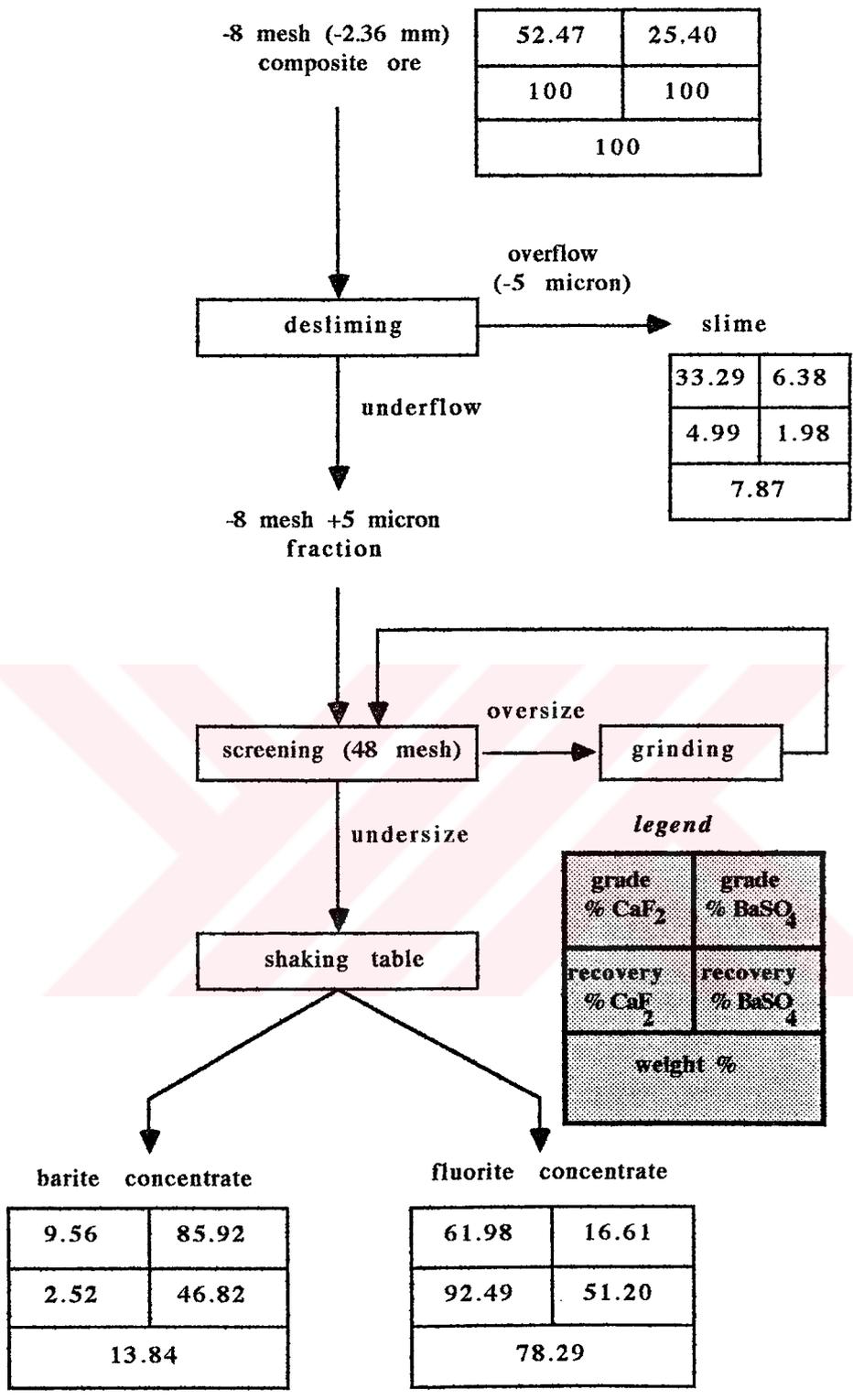


Figure 3. Gravity Concentration of deslimed Composite Ore Ground to -48 mesh (-295 μm)

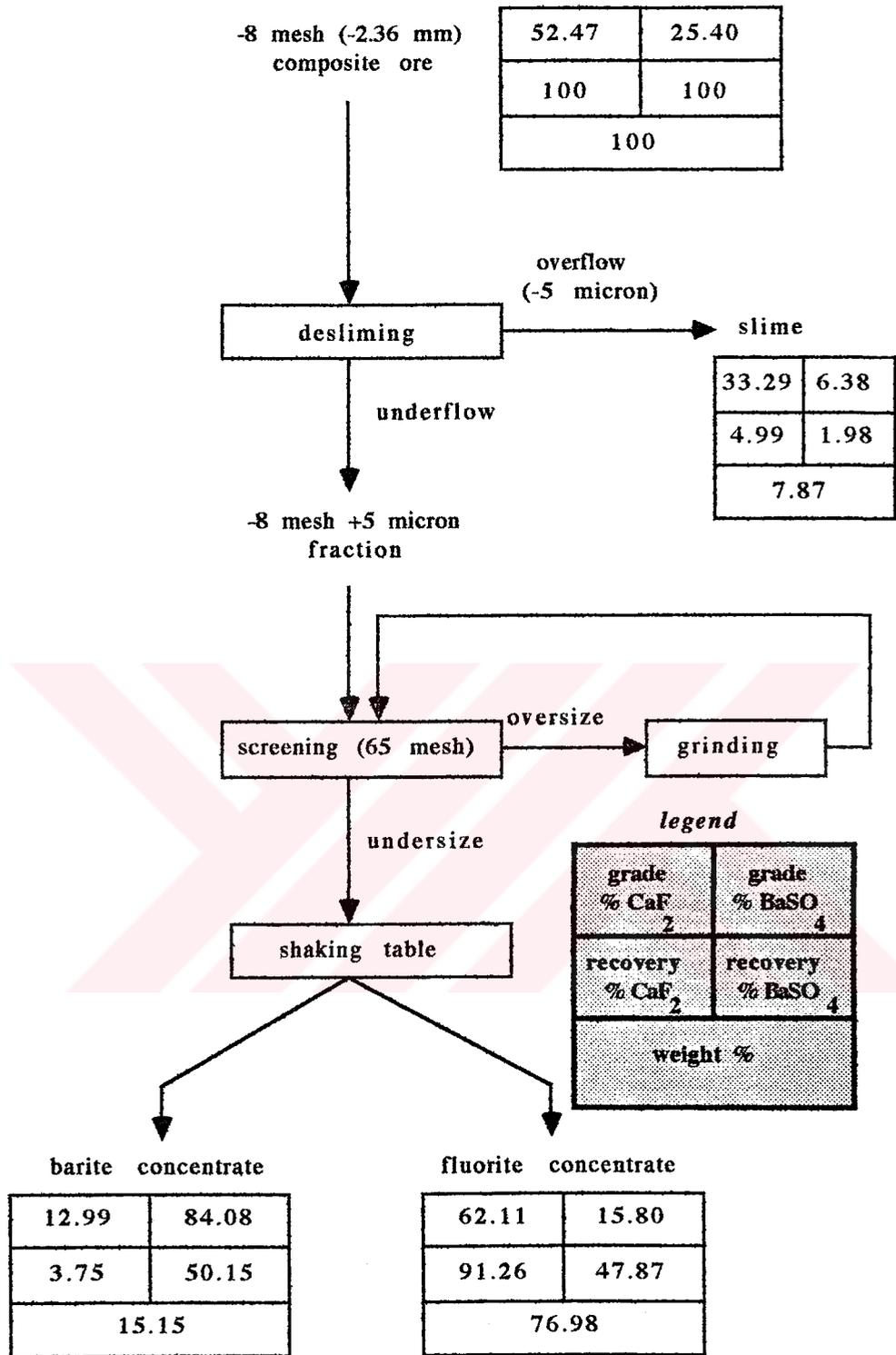


Figure 4. Gravity Concentration of deslimed Composite Ore Ground to -65 mesh (-208 μm)

fluorite concentrate of 62.11% CaF_2 with 91.26% recovery were produced.

Another test was carried out without removing the slime from the composite ore. The composite ore was again ground to -65 mesh (-208 micron) with close control. Barite concentrate of 78.55% BaSO_4 with 54.22% recovery, and fluorite concentrate of 60.07% CaF_2 with 94.42% recovery were obtained by tabling (Figure 5). The results were close to the results obtained by the separation of slime prior to grinding of composite ore. Slime is rich in rare earth element content, and poor in barite-fluorite contents. Therefore, the slime was separated for the production of rare earth elements and also not to reduce the separation efficiency.

5.1.3 Gravity Concentration of Composite Ore without Grinding

The idea in the development of this flowsheet was based on the mineral distributions of composite sample in screen fractions given in Table 3. Screen fractions coarser than 65 mesh (208 micron) are rich in fluorite, and finer fractions than 65 mesh (208 micron) are rich in barite minerals due to the friability of it. Therefore, -8 mesh (-2362 μm) composite ore was firstly sieved through 65 mesh (208 μm) screen. -8 +65 mesh (-2362 +208 μm) fraction was tried to be concentrated by jigging, and -65 mesh (-208 μm) fraction was concentrated by shaking table after separating from slime by hydrocyclone (Figure 6).

Because of the low concentration criterion and insufficient liberation of minerals at -8 +65 mesh (-2362 +208 μm) fraction, concentration of barite and fluorite minerals in this fraction by jigging was not successful. On the other hand -65 mesh (-208 μm) fraction was concentrated and two barite

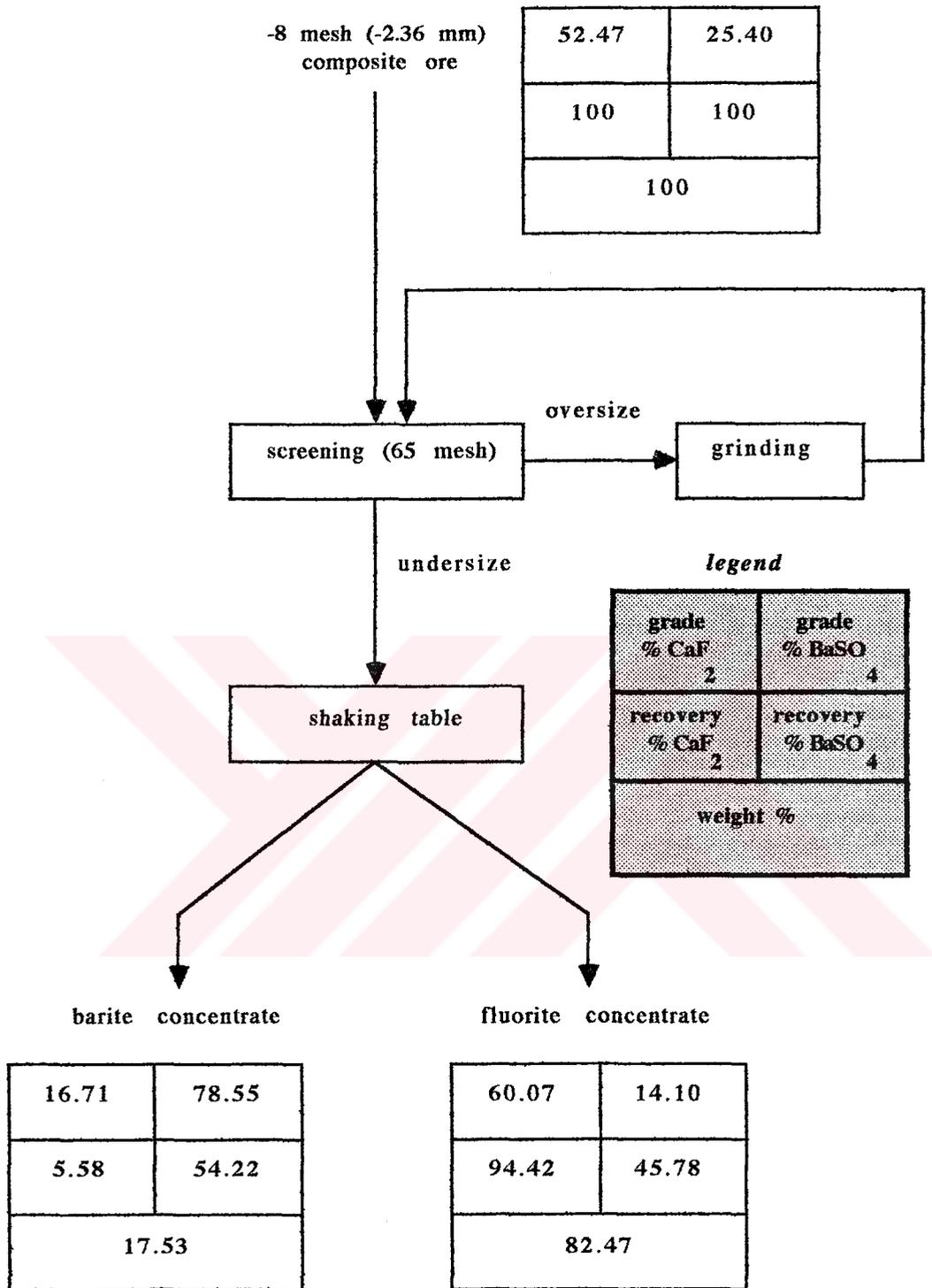


Figure 5. Gravity Concentration of Composite Ore Ground to -65 mesh (-208 μm)

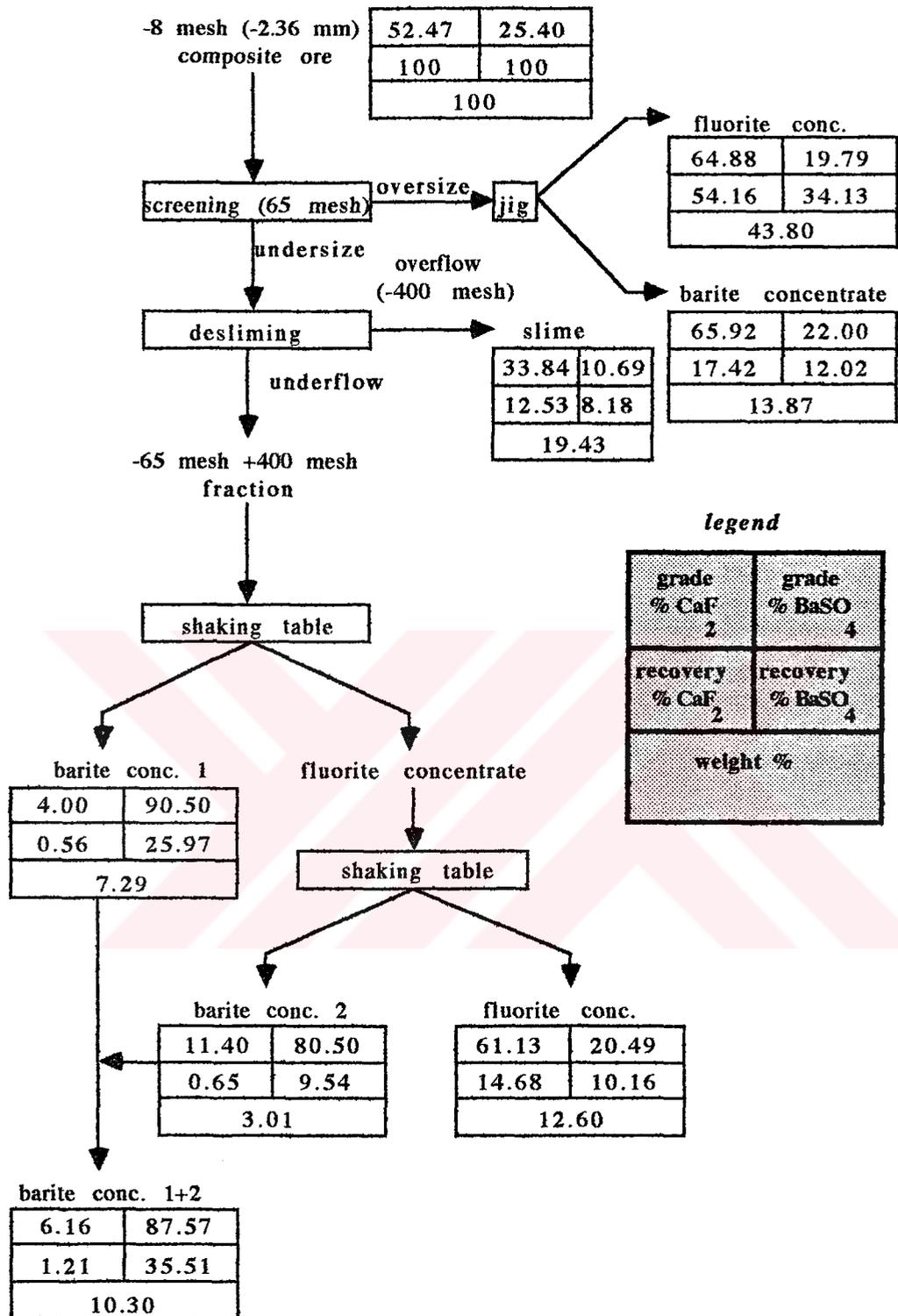


Figure 6. Gravity Concentration of Composite Ore without Grinding

concentrates having 90.50% BaSO₄ and 80.50% BaSO₄ grades, were obtained by shaking table. Drilling mud grade barite can be obtained when these two concentrates combined. The grade and the recovery of the combined concentrate are 87.57% BaSO₄ and 35.51% respectively. Fluorite concentrates obtained in the test were poor in both grade and recovery as shown in Figure 6, since -65 mesh (-208 μm) fraction was already poor in fluorite content.

5.1.4 Gravity Concentration of Composite Ore with the Grinding of +65 mesh (+208 micron) Fraction

After the sieving of composite ore through -65 mesh (208 μm) screen, -65 mesh (-208 μm) fraction was concentrated by means of shaking table. To provide better liberation of barite and fluorite particles, +65 mesh (+208 μm) fraction was ground to -35 mesh (-417 μm) under close control and fed to shaking table for concentration (Figure 7).

The results of this experiment proved that grinding of the -8 +65 mesh (-2362 +208 μm) fraction to -35 mesh (-417 μm) under close control, gave better grades and recoveries in shaking table test. Barite concentrate had 73.00% BaSO₄ grade with 24.63% recovery, and fluorite concentrate had 74.80% CaF₂ grade with 70.00% recovery.

The combined concentrate of fluorites had a grade of 72.00% CaF₂ with 84.68% recovery, while the combined concentrate of barites had a grade of 80.95% BaSO₄ with 60.14% recovery (Figure 7). The combined fluorite concentrate was a marketable product as flux.

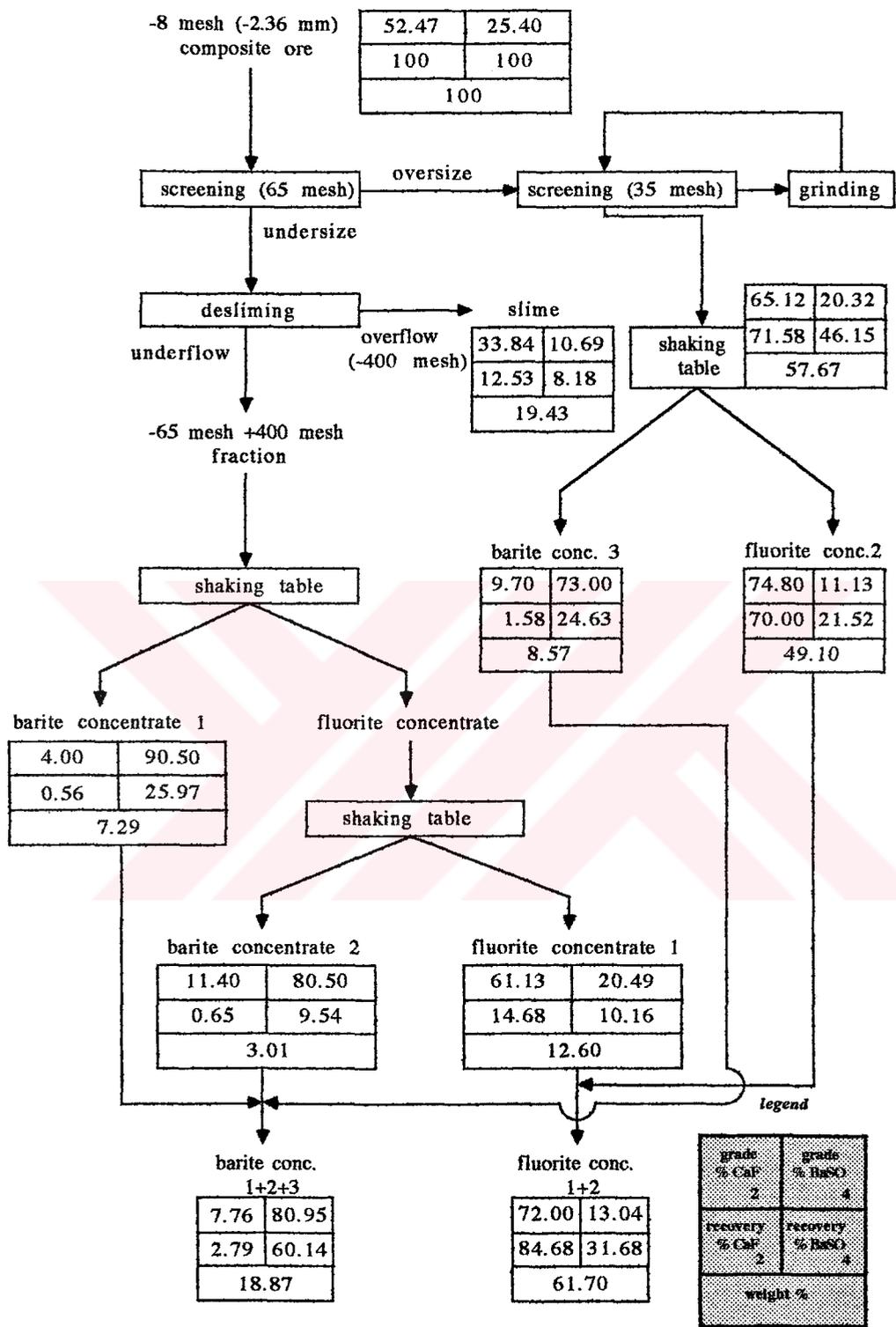


Figure 7. Gravity Concentration of Composite Ore with the Grinding of +65 mesh (+208 μm) Fraction

5.2 Flotation Studies

Flotation studies were performed on composite ore ground to -65 mesh (-208 μm) size. Flotation of barite and fluorite minerals was studied separately.

5.2.1 Flotation of Fluorite

In this group of studies, barite was tried to be depressed, and fluorite was tried to be floated. First experiment was performed at pH 9 by using 400 g/ton of AlCl_3 , 400 g/ton of Na_2SiO_3 as depressants, 600 g/ton of A723 type collector (Cyanamid company), and 65 g/ton of MIBC as frother. Conditioning times were 10 minutes for depressants, and 5 minutes for collectors. Fluorite concentrate obtained at the end of 5 minutes flotation time was cleaned by adding 180 g/ton of AlCl_3 and 180 g/ton of Na_2SiO_3 . No collector was used at this stage. The results were given in Figure 8.

The same experiment was repeated by using hot flotation pulp (50°C). Cleaning stage was not applied. The results were given in Figure 9.

The results of the both tests showed that, the grades of the fluorite and barite in their respective concentrates increased too little, and reagents used for the selective flotation of fluorite were unsuccessful to provide the selectivity between fluorite and barite minerals.

5.2.2 Flotation of Barite

In order to obtain the selectivity between barite and fluorite minerals in flotation, barite flotation tests were carried out. In the first experiment 400 g/ton of Na_2SiF_6 as fluorite

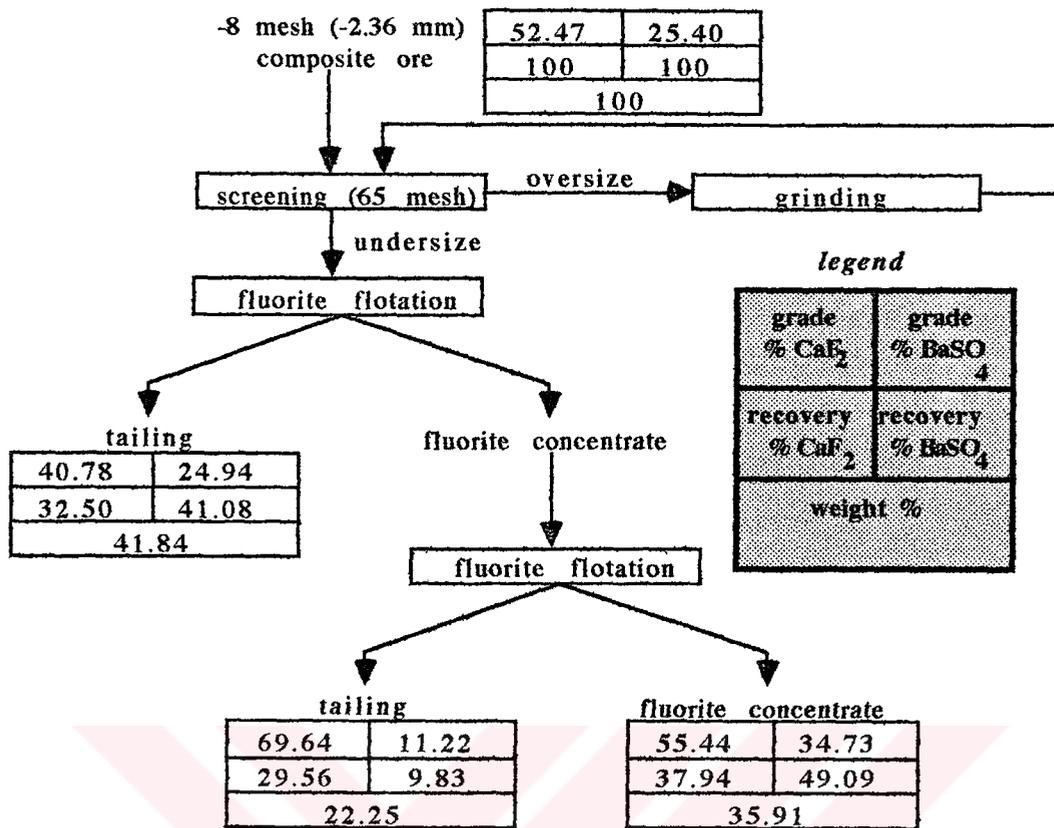


Figure 8. Flotation of Fluorite from Composite Ore

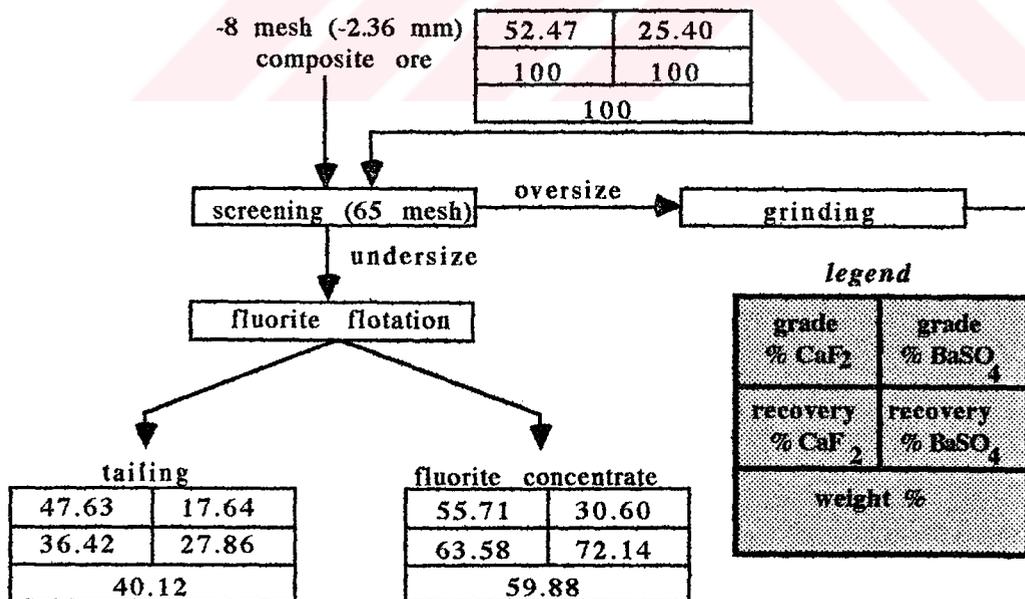


Figure 9. Flotation of Fluorite from Composite Ore (Hot Pulp)

depressant, and 200 g/ton of A845 collector (Cyanamid company) for barite were used at pH 9.3. Frother was 65 g/ton of MIBC. Conditioning times for depressant and collector were 10 and 5 minutes respectively. Flotation time was 5 minutes. The results were given in Figure 10.

To increase the grade and recovery of the flotation concentrates, the above experiment was repeated by increasing the amount of Na_2SiF_6 to 600 g/ton, and amount of A845 to 400 g/ton. pH of the pulp was 9.2. The results were given in Figure 11.

The results of the both experiments showed that, more selective fluorite concentrates with higher recoveries were obtained by reverse flotation than direct flotation. Drilling mud grade barite was not obtained during fluorite and barite flotation studies. But, the fluorite concentrates obtained by reverse flotation was suitable for metallurgical uses (Figure 10, 11).

5.2.2.1 Effect of pH on Barite Flotation for Fluorite Concentration

In order to examine the effect of pH on fluorite grade and recovery, eight flotation experiments were carried out at pH ranges varying from 4 to 11. The natural pH of the flotation pulp was measured as 8.0. During the tests, acidity and basicity of the pulp was adjusted by the addition of HCl and NaOH respectively. 850 g/ton of reagent S-3903 was used as barite collector, and 65 g/ton of MIBC was used as frother. No depressants was added to the flotation pulp. Conditioning time for collector was 20 minutes, and flotation time was 10 minutes. The results of these tests were given in Table 4 and Figure 12. From these results, optimum pH of barite flotation

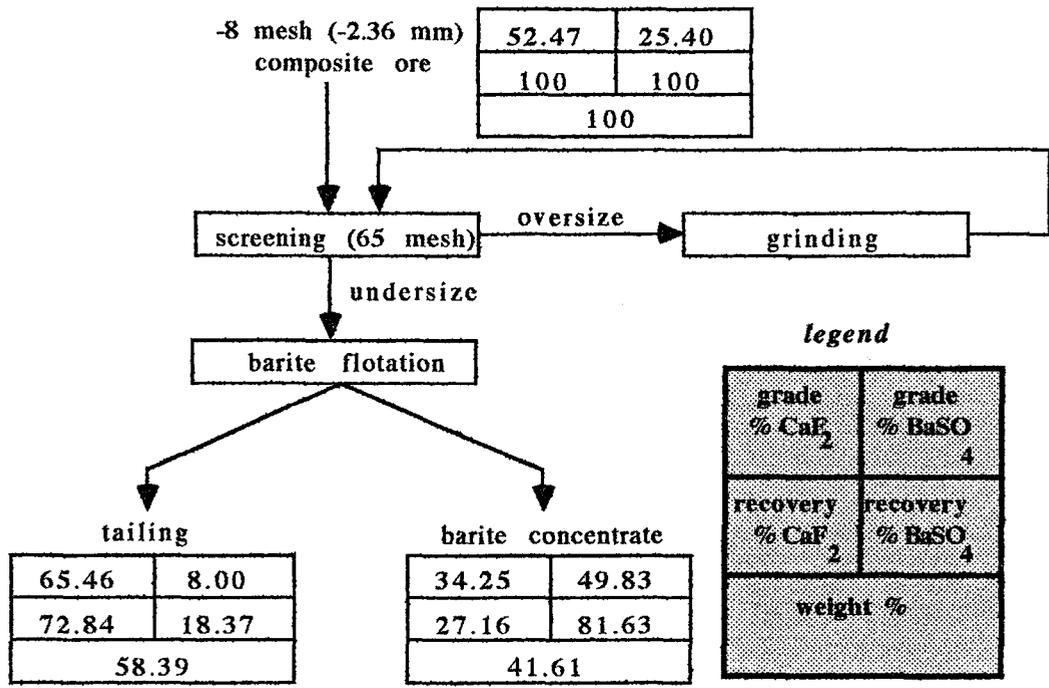


Figure 10. Flotation of Barite from Composite Ore

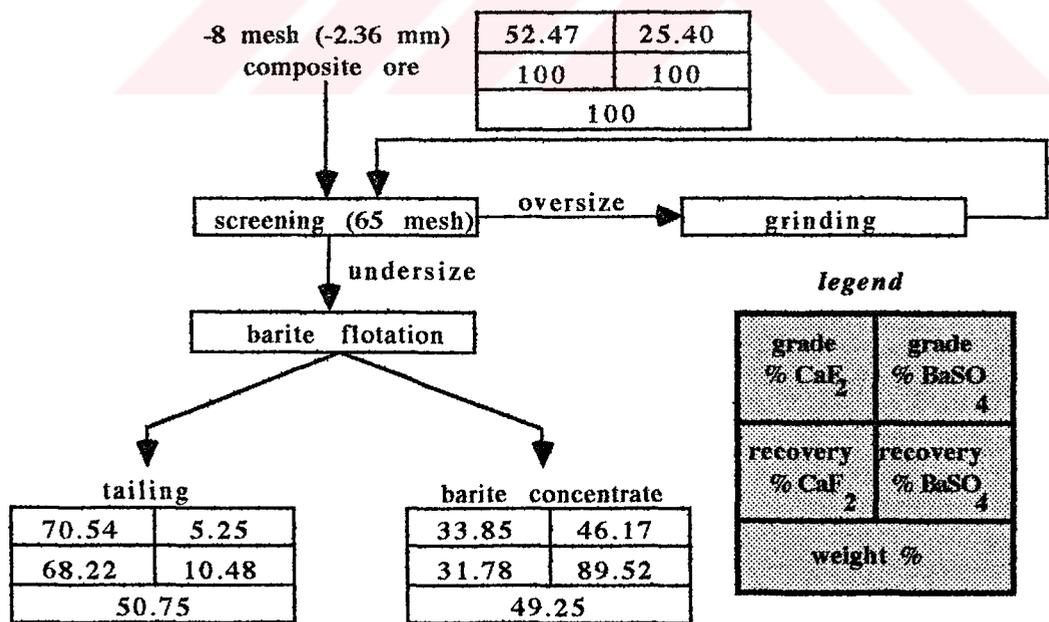


Figure 11. Flotation of Barite from Composite Ore

Table 4. Effect of pH on Barite Flotation for Fluorite Concentration

pH	Fluorite concentrate (depressed)				Barite concentrate (floated)			
	grade (%)		recovery(%)		grade(%)		recovery(%)	
	CaF ₂	BaSO ₄	CaF ₂	BaSO ₄	CaF ₂	BaSO ₄	CaF ₂	BaSO ₄
4	56.15	28.01	88.32	91.02	35.08	13.06	11.68	8.98
5	56.10	27.82	87.39	89.54	36.22	14.55	12.61	10.46
6	56.40	27.90	84.44	86.29	38.07	16.24	15.56	13.71
7	58.50	25.49	78.94	71.06	37.85	25.17	21.06	28.94
8	62.65	20.46	76.18	51.39	34.53	34.11	23.82	48.61
9	64.65	17.93	71.17	40.76	35.81	35.62	28.83	59.24
10	64.75	14.72	59.33	27.86	41.10	35.29	40.67	72.14
11	68.15	12.32	51.81	19.35	42.06	34.08	48.19	80.65

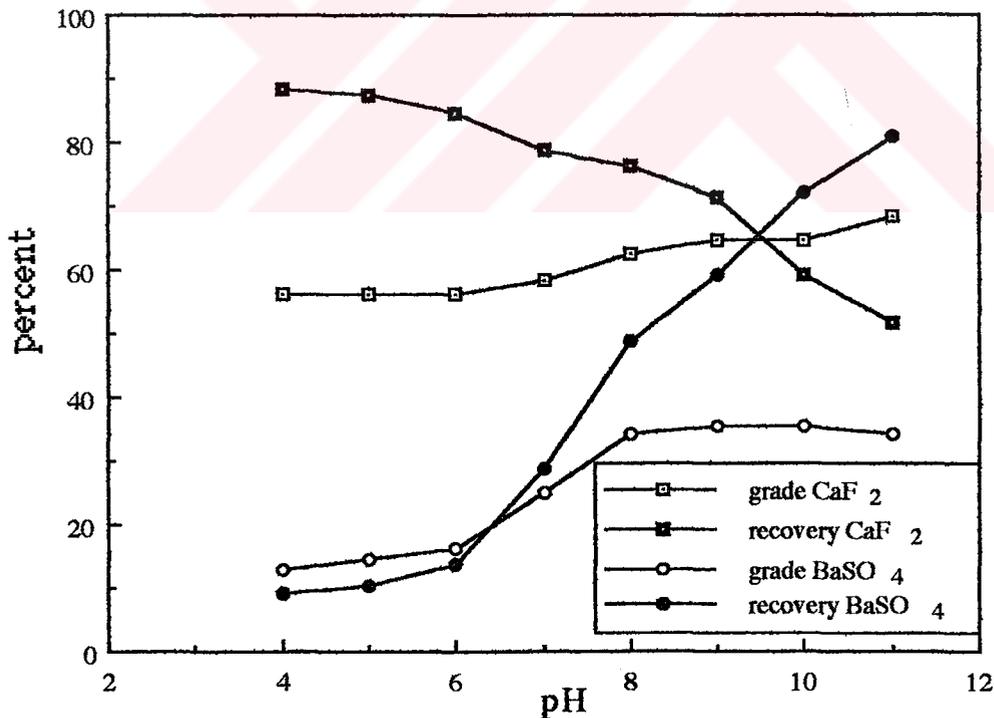


Figure 12. Effect of pH on Barite Flotation for Fluorite Concentration

for fluorite concentration was found as 8, since at this pH the CaF_2 grade of barite concentrate (floated) was minimum.

5.3 Concentration Studies Performed by the Combination of Gravity Concentration and Flotation

In this group of studies, in order to obtain higher grade fluorite concentrates with higher recoveries, the combination of gravity concentration and flotation was used. Therefore, fluorite concentrates obtained from shaking table were concentrated by flotation.

5.3.1 Pre-Concentration by Gravity Method

In the gravity concentration part of this method, composite ore was ground to -65 mesh (-208 μm) size under close control, and directly fed to tabling. The grade and recovery of the barite pre-concentrate were 78.55% BaSO_4 and 54.22% respectively, also the grade and recovery of the fluorite pre-concentrate were 60.07% CaF_2 and 94.42% respectively (Figure 13).

The results obtained by gravity concentration studies showed that drilling grade barite concentrate could be obtained easily, therefore in this method studies were targeted to fluorite.

5.3.2 Upgrading of Fluorite Pre-Concentrate by Flotation

In order to obtain higher grade fluorite concentrates, reverse flotation was applied to shaking table fluorite pre-concentrate at three different flotation conditions. By using 400

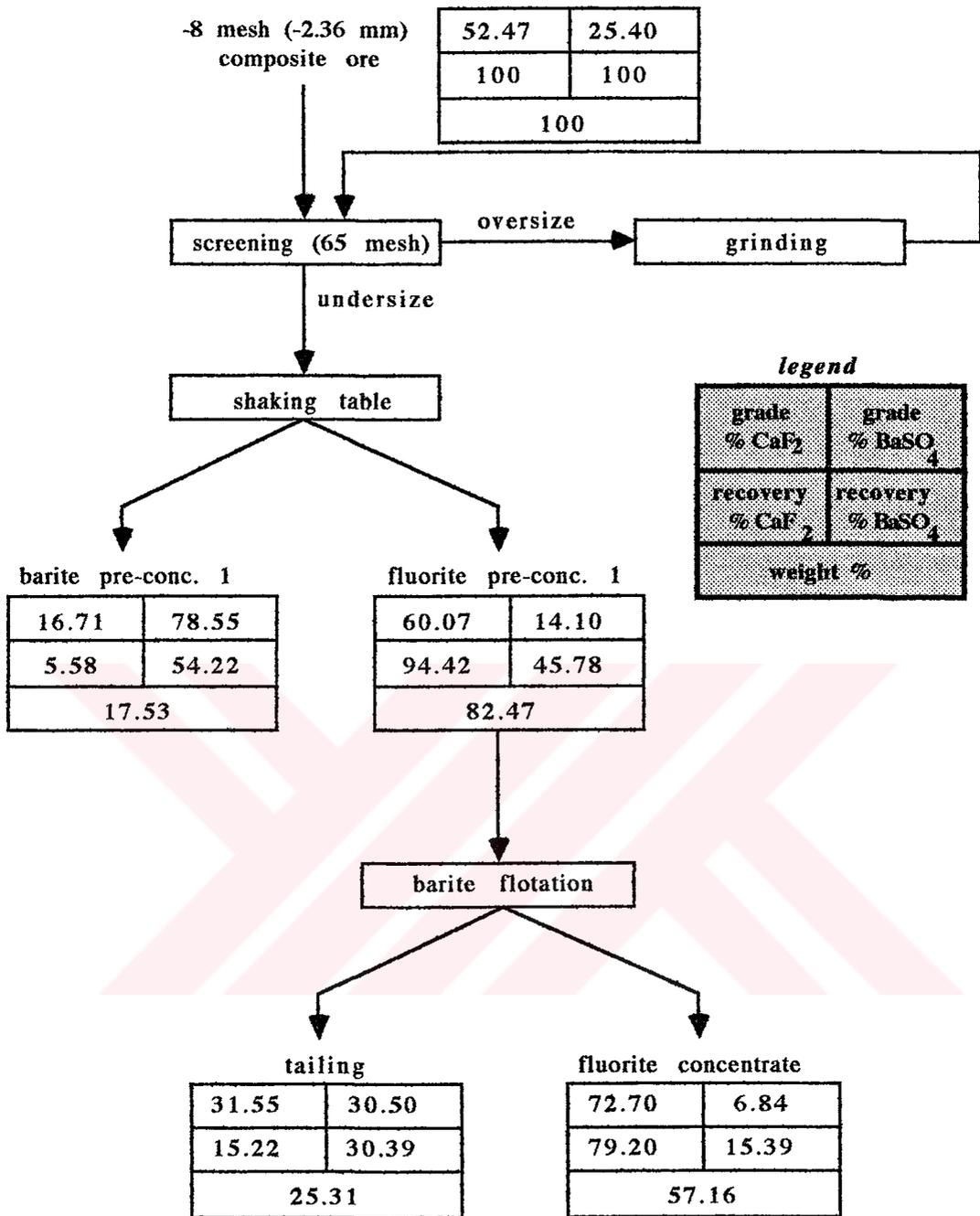


Figure 13. Upgrading of Fluorite Pre-Concentrate by Reverse Flotation

g/ton of A845 and 150 g/ton of sodium oleate barite flotation tests were performed. During these tests, 400 g/ton of Na_2SiO_3 , 400 g/ton of Na_2CO_3 , and 400 g/ton of Na_2SiF_6 were used. Tests were made at pH 7.6. Because of frothing property of sodium oleate, no frother was used in the test performed with sodium oleate. On the other hand, 65 g/ton of MIBC was used in the test performed with A845. Conditioning times were 10 minutes for depressants, and 5 minutes for collectors. Results were given in Table 5.

Metallurgical grade fluorite concentrates were obtained in both tests, but A845 gave higher grade and recovery than sodium oleate.

In order to obtain high grade fluorite concentrate with high recovery, three stage flotation was applied in another test. For this purpose barite was tried to be floated from shaking table fluorite pre-concentrate by using 220 g/ton of sodium oleate. The fluorite concentrate obtained was tried to be upgraded by again reverse flotation with 320 g/ton of amine D-acetate. Final upgrading was made by applying fluorite flotation with 640 g/ton of A723 collector. The grade of the fluorite concentrate was increased to 75.00% CaF_2 with a recovery of 59.61%.

Table 5. Effect of Type of Collector on Fluorite Concentrate

Type of collec.	Fluorite Concentrate (depressed)				Barite Concentrate (floated)			
	grade (%)		recovery(%)		grade (%)		recovery(%)	
	CaF_2	BaSO_4	CaF_2	BaSO_4	CaF_2	BaSO_4	CaF_2	BaSO_4
sodium oleate	69.10	9.77	61.96	18.10	48.08	19.85	32.46	27.68
A845	72.70	6.84	79.20	15.39	31.55	30.50	15.22	30.39

The optimum results were given in Table 5 and in Figure 13.

5.4 Concentration Studies Performed by the Combination of Gravity Concentration-Flotation-Magnetic Separation Techniques

Barite and fluorite pre-concentrates obtained by shaking table were tried to be upgraded by applying barite flotation followed by high intensity magnetic separation to remove magnetic impurities. Two different alternatives were developed in this group of studies.

5.4.1 Alternative I

5.4.1.1 Gravity Concentration Part

In the first method, composite ore was ground to -65 mesh (-208 μm) size with close control. Ground ore was deslimed by the aid of hydrocyclone. -65 +400 mesh (-208 +37 μm) fraction obtained as hydrocyclone underflow was concentrated by tabling. Barite pre-concentrate 1 assaying 91.89% BaSO_4 with 47.61% recovery, barite pre-concentrate 2 assaying 78.99% BaSO_4 with 12.65% recovery, and fluorite pre-concentrate 2 assaying 77.06% CaF_2 with 67.50% recovery were obtained. The flowsheet and the results of this test were given in Figure 14.

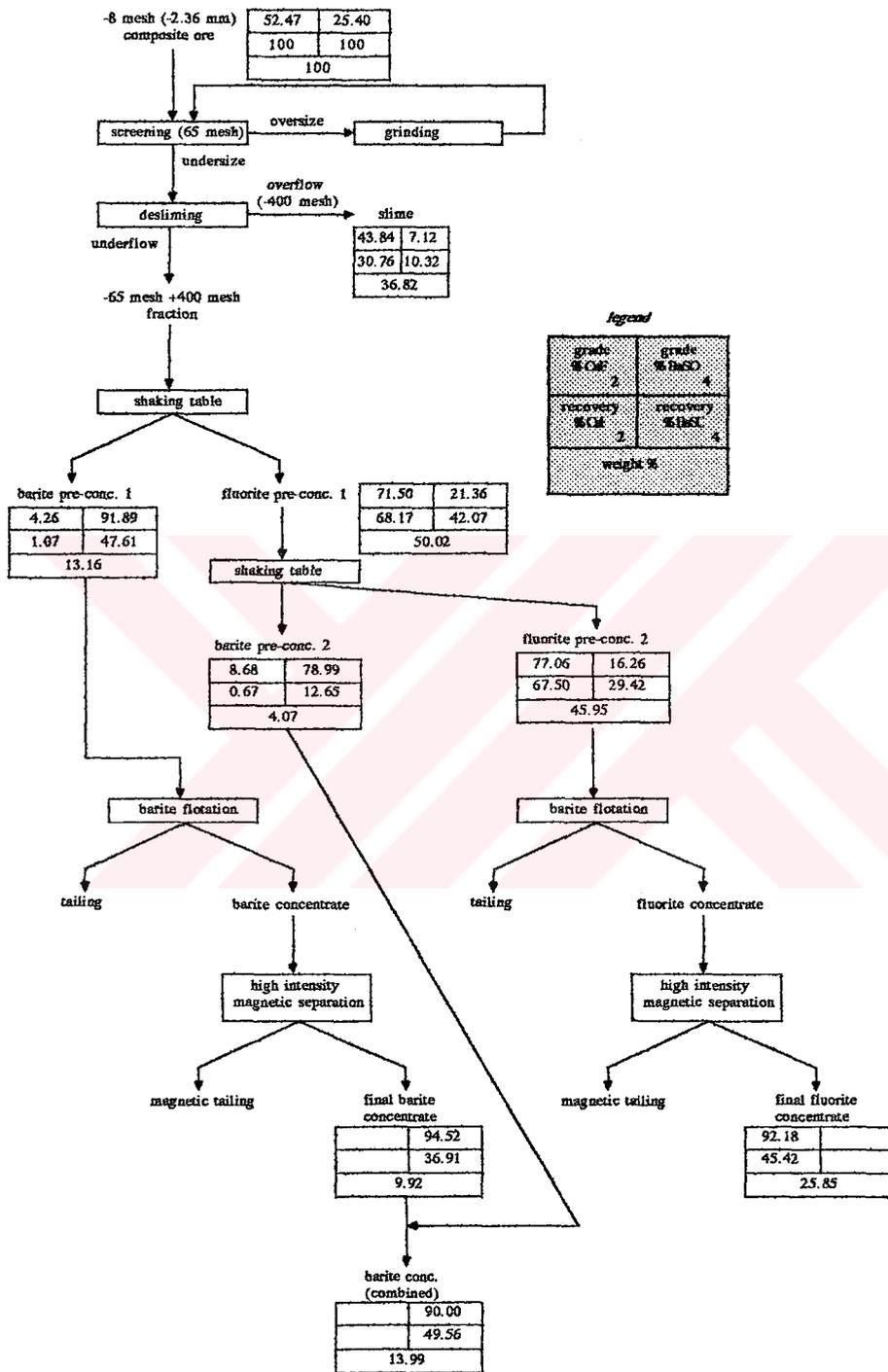


Figure 14. The Flowsheet and the Optimum Results of Alternative I

5.4.1.2 Upgrading of Fluorite Pre-Concentrate by Flotation and High Intensity Magnetic Separation

Shaking table fluorite pre-concentrate 2 (Figure 14) was concentrated by reverse flotation. In the flotation tests, collectors for barite, and depressants for fluorite were used. The first flotation experiment was made by using 1250 g/ton of Na_2SiF_6 , 1250 g/ton of Na_2CO_3 , and 150 g/ton of sodium oleate as barite collector at pH 7.8. Conditioning times were 30 and 15 minutes for depressants and collector respectively. Final fluorite concentrate after high intensity magnetic separation contained 83.58% CaF_2 , and the recovery was 27.77%.

In the second flotation experiment, 750 g/ton of Na_2CO_3 , 750 g/ton of Na_2SiO_3 , 750 g/ton of Na_2SiF_6 were added to the flotation pulp at pH 8.0 to depress fluorite. After conditioning for 10 minutes, 300 g/ton of alkyl succinamate type A845 collector (from Cynamid company) was added as collector for barite. Conditioning time for collector was kept as 5 minutes. Frother was 65 g/ton of MIBC (methyl isobutyl carbinol). Magnetic impurities were removed from the flotation fluorite concentrate by high intensity magnetic separation. The grade and the recovery of the final fluorite concentrate were 91.36% CaF_2 and 47.54% respectively.

In the third flotation test, 1250 g/ton of Na_2SiF_6 , 1000 g/ton of Na_2CO_3 were used as depressants for fluorite, and 250 g/ton of A845 was used as barite collector at pH 7.7. In order to prevent the depression of silicates, Na_2SiO_3 was not used. Conditioning times, frother type and amount were kept as in the first experiment. After high intensity magnetic separation a fluorite concentrate assaying 92.18% CaF_2 with 45.42% recovery was obtained (Figure 14).

The next experiment was carried out by not only increasing depressant amount but also collector amount. 1250 g/ton of Na_2SiF_6 , 1250 g/ton of Na_2CO_3 were used as fluorite depressants, and 350 g/ton of A845 was used as barite collector at pH 7.9. Conditioning times for depressants and collector were increased to 30 and 15 minutes respectively. Final fluorite concentrate obtained after high intensity magnetic separation assayed 90.34% CaF_2 with a recovery of 46.68%. This experiment was repeated by increasing Na_2CO_3 amount from 1250 g/ton to 2250 g/ton and keeping the other parameters fixed. Increasing the Na_2CO_3 amount was also resulted in increase of pulp pH to 8.6. A fluorite concentrate assaying 84.32% CaF_2 with 39.28% recovery was obtained at the end of high intensity magnetic separation. The results showed that, an increase in the amount of Na_2CO_3 reduced the both grade and recovery of the fluorite concentrate.

The results of these experiments showed that the use of A845 instead of sodium oleate as barite collector increased selectivity and so the grade and recovery of fluorite concentrate.

5.4.1.3 Upgrading of Barite Pre-Concentrate by Flotation and High Intensity Magnetic Separation

Barite pre-concentrate 1 obtained by shaking table (Figure 14) was tried to be upgraded by the combination of barite flotation and high intensity magnetic separation. The first experiment was carried out with the use of 750 g/ton of Na_2CO_3 , 750 g/ton of Na_2SiO_3 , 750 g/ton of Na_2SiF_6 for the depression of gangue minerals, and 400 g/ton of A845 for the flotation of barite, at pH 8.6. Conditioning times were 30 and 15 minutes for depressants and collector respectively. Frother was 65 g/ton of MIBC. Barite flotation concentrate was cleaned

from magnetic impurities by high intensity magnetic separation. Final barite concentrate assayed 93.34% BaSO₄ with 36.38% recovery. By increasing the amount of the depressants to 1250 g/ton and decreasing the amount of the collector to 350 g/ton, a similar experiment was carried out at pH 8.7. The obtained barite concentrate was upgraded by a second flotation with the addition of 500 g/ton of Na₂CO₃, 500 g/ton of Na₂SiO₃, 500 g/ton of Na₂SiF₆, and 300 g/ton of A845 as collector. The grade of the final barite concentrate obtained from the high intensity magnetic separation was increased to 94.49% BaSO₄, while the recovery was reduced to 31.40%.

Sodium oleate was also used as barite collector instead of A845. In order to provide the selectivity between barite and gangue minerals during flotation, amounts of depressants were increased to 1500 g/ton, and collector amount was decreased to 260 g/ton. Final barite concentrate assaying 94.52% BaSO₄ with 36.91% recovery was obtained when pH was 8.9 (Figure 14).

Flotation and high intensity magnetic separation were not applied to shaking table barite pre-concentrate 2, in order to prevent the recovery loss. The optimum final fluorite concentrate was marketable as No. 2 ceramic grade fluorite. On the other hand, the optimum final barite concentrate was also suitable for chemical manufacturing or drilling mud which the specific gravity of this concentrate was 4.46.

5.4.2 Alternative II

5.4.2.1 Gravity Concentration Part

The concept of the second alternative developed was based on the concentration of +65 (+208 μm) and -65 mesh (-208 μm) fractions of the composite ore separately. For this purpose, composite ore was firstly sieved through 65 mesh

(208 μm) sieve. -65 mesh (-208 μm) fraction was deslimed by hydrocyclone. -65 +400 mesh (-208 +37 μm) fraction obtained from hydrocyclone underflow was concentrated by tabling. Barite pre-concentrate 1 assaying 91.60% BaSO_4 with 31.91% recovery, and fluorite pre-concentrate 1 assaying 51.53% CaF_2 with 15.57% recovery were obtained. On the other hand, +65 mesh (+208 μm) fraction was ground to -35 mesh (-417 μm) size with close control, and was deslimed by hydrocyclone. -35 +400 mesh (-417 +37 μm) fraction was separated into two fractions as -35 +65 mesh (-417 +208 μm) and -65 +400 mesh (-208 +37 μm) fractions. These fractions were fed to shaking table separately. Barite pre-concentrate 2 assaying 72.29% BaSO_4 with 5.92% recovery, and fluorite pre-concentrate 2 assaying 73.58% CaF_2 with 35.70 recovery were produced by tabling of -35 +65 mesh (-417 +208 μm) fraction. The grade and recovery of barite pre-concentrate 3 obtained from -65 +400 mesh (-208 +37 μm) fraction were 85.96% BaSO_4 and 11.78% respectively. Also, the grade and recovery of fluorite pre-concentrate 3 obtained from -65 +400 mesh (-208 +37 μm) fraction were 67.70% CaF_2 and 16.12% respectively (Figure 15).

5.4.2.2 Upgrading of Fluorite Pre-Concentrate by Flotation and High Intensity Magnetic Separation

Fluorite pre-concentrate 1 was upgraded to 89.66% CaF_2 with 12.73% recovery by applying reverse flotation and high intensity magnetic separation. During the flotation, 1250 g/ton of Na_2SiF_6 , 1500 g/ton of Na_2CO_3 , and 250 g/ton of A845 were used at pH 7.7. Flotation pulp was conditioned 15 minutes for depressants, and 5 minutes for collector.

Fluorite pre-concentrate 2 was concentrated by the same way. Only the amount of Na_2CO_3 was increased to 2000 g/ton which caused the increase of pH to 8.0. After high

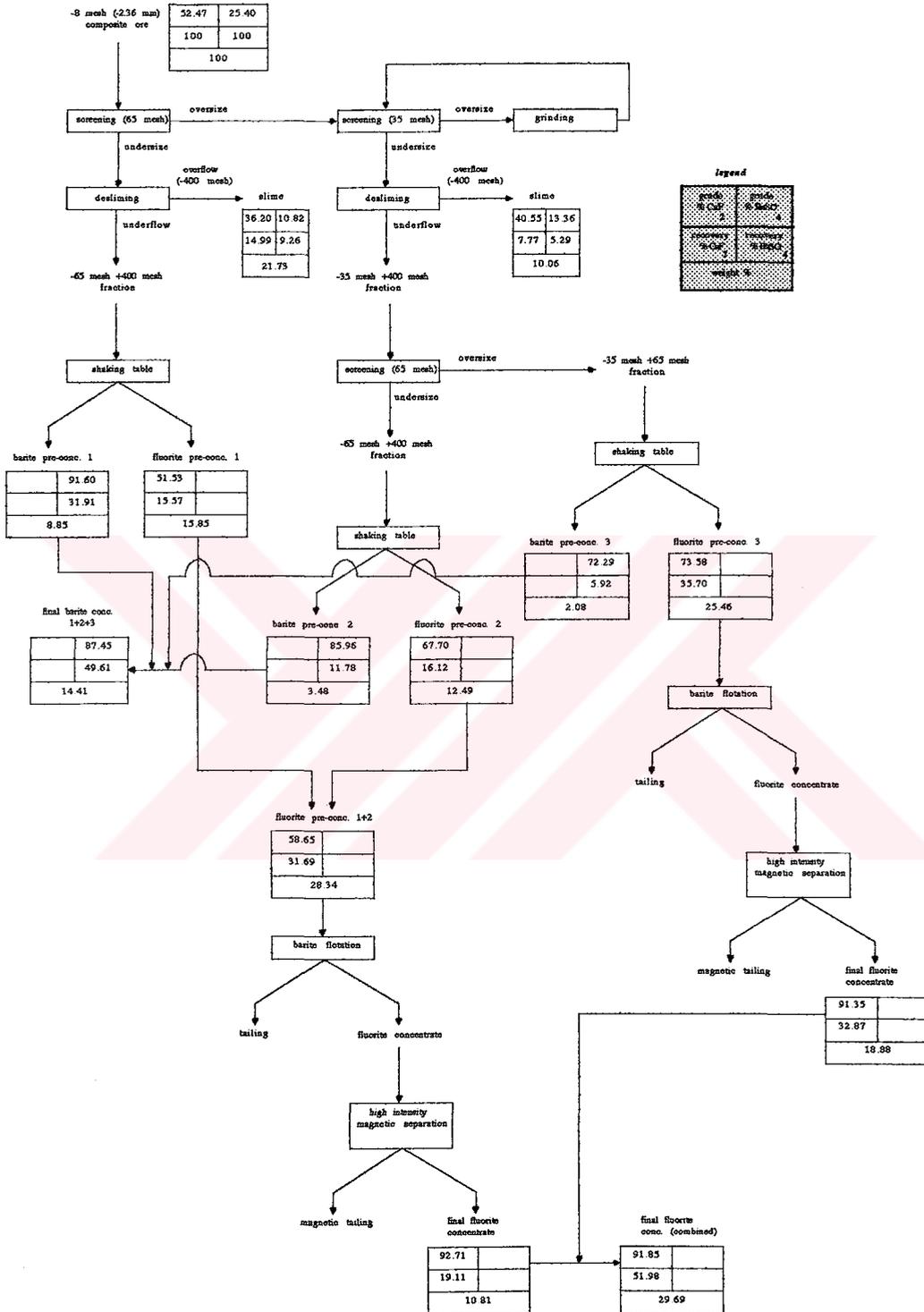


Figure 15. The Flowsheet and the Optimum Results of Alternative II

intensity magnetic separation, final fluorite concentrate assaying 79.72% CaF₂ with 6.97% recovery was obtained.

The grade of fluorite pre-concentrate 3 was increased to 85.30% CaF₂ with 33.08% recovery by applying reverse flotation and high intensity magnetic separation. During the flotation, 1250 g/ton of Na₂SiF₆, 1500 g/ton of Na₂CO₃, and 250 g/ton of A845 were used at pH 7.7. Conditioning times were 15 minutes for depressants, and 5 minutes for collector. Another experiment on this sample was made by using 1250 g/ton of Na₂SiF₆, 750 g/ton of Na₂CO₃, and 350 g/ton of A845 at pH 7.6. Conditioning times were increased to 30 minutes for depressants, and 10 minutes for collector. At the end of high intensity magnetic separation, final fluorite concentrate assaying 86.43% CaF₂ with 31.01% recovery was obtained. In another experiment, the use of 150 g/ton of A845 and 150 g/ton of sodium oleate combination, keeping the other parameters constant, increased the grade of the final concentrate to 87.95% CaF₂ with 31.84% recovery. The best result was obtained by using 1250 g/ton of Na₂SiF₆, 2750 g/ton of Na₂CO₃, and 600 g/ton of S-3903 collector at pH 8.9. Conditioning time for S-3903 was 20 minutes. Final concentrate had 91.35% CaF₂ grade and 32.87% recovery (Figure 15).

Fluorite pre-concentrates 1 and 2 were combined for flotation and high intensity magnetic separation studies. In the first experiment, combined sample was conditioned for 15 minutes with 1250 g/ton of Na₂SiF₆ and 1500 g/ton of Na₂CO₃. Reverse flotation was performed at pH 8.2 by adding 250 g/ton of A845 and conditioning for 5 minutes. Final concentrate of high intensity magnetic separation assayed 90.29% CaF₂ with 11.70% recovery.

In the second experiment with fluorite pre-concentrate 1+2, 1250 g/ton of Na₂SiF₆ and 750 g/ton of Na₂CO₃, and 350 g/ton of A845 were used. Conditioning times

were 30 and 10 minutes for depressants and collector respectively. pH of the flotation pulp was 7.6. High intensity magnetic separation produced a final concentrate having 90.91% CaF₂ with 18.63% recovery.

Another experiment was made by only increasing the amounts of Na₂SiF₆ to 2000 g/ton, and Na₂CO₃ to 1500 g/ton. The grade and recovery of the final concentrate were 87.09% CaF₂ and 13.99% respectively.

At pH 9.0 by using 1250 g/ton of Na₂SiF₆ and 3000 g/ton of Na₂CO₃, and 600 g/ton of S-3903, reverse flotation was applied to combined sample (fluorite pre-concentrates 1+2). Conditioning times were 40 and 20 minutes for depressants and collector respectively. Final concentrate obtained after high intensity magnetic separation was upgraded to 89.82% CaF₂ with 14.06% recovery. The best result was obtained by using 1250 g/ton of Na₂SiF₆, 750 g/ton of Na₂CO₃, and 900 g/ton of S-3903 collector at pH 7.6. Stage addition of collector to the flotation pulp was applied. The grade and recovery of the final concentrate were 92.71% CaF₂ and 19.11% respectively (Figure 15).

When final fluorite concentrates were combined, the grade and recovery of the final concentrate reached to 91.85% CaF₂ and 51.98% respectively (Figure 15).

5.4.2.3 Upgrading of Barite Pre-Concentrates

In order to prevent recovery losses, flotation and high intensity magnetic separation studies were not performed on barite pre-concentrates 1, 2, and 3. When these three pre-concentrates were combined, final barite concentrate assaying 87.45% BaSO₄ with 49.61% recovery was obtained (Figure 15).

The optimum final fluorite concentrate (combined) was marketable as No. 2 ceramic grade fluorite. On the other hand, optimum final barite concentrate (combined) was also marketable as drilling mud which the specific gravity of this concentrate was 4.36.

Among the two alternatives applied, the first alternative gave the highest barite and fluorite grades while the second alternative gave the highest barite and fluorite recovery (Figure 14, Figure 15).

5.5 Concentration Studies Performed by the Combination of Flotation and Magnetic Separation Techniques

Concentration studies performed by the combination of flotation and magnetic separation techniques were carried out on composite ore ground to -65 mesh (-208 μm) size. Barite and fluorite concentrates obtained from flotation were upgraded by high intensity magnetic separation to remove magnetic impurities.

The first experiment was made at pH 7.9 (natural pH) by using 750 g/ton of Na_2SiF_6 , 750 g/ton of Na_2SiO_3 , 750 g/ton of Na_2CO_3 , and 600 g/ton of S-3903 type collector for barite flotation. Collector was used in the amounts of 350 g/ton, 100 g/ton, and 150 g/ton. Conditioning time for depressants was 30 minutes. For collector, 20 and 10 minutes conditioning times were applied. After cleaning the magnetic impurities, the grade of the fluorite concentrate was increased to 82.58% CaF_2 with 39.77% recovery, but the grade of the barite concentrate was still too low as 34.54% BaSO_4 with 60.99% recovery.

In the second experiment, at pH 7.9 1250 g/ton of Na_2SiF_6 , 750 g/ton of Na_2CO_3 , and 450 g/ton of S-3903 (as 300 g/ton and 150 g/ton) were used. Fluorite concentrate obtained

was again conditioned with 750 g/ton of Na_2SiF_6 and 500 g/ton of Na_2CO_3 for 10 minutes, and by using 250 g/ton of S-3903 (as 150 g/ton and 100 g/ton) barite flotation was applied. Similar results to the first experiment were obtained after the high intensity magnetic separation, the grade of the fluorite concentrate was 79.89% CaF_2 with 38.73% recovery.

The third experiment was carried out at pH 7.9 by using 600 g/ton of S-3903 collector. After 20 minutes conditioning time barite flotation was applied. Fluorite concentrate obtained was conditioned with 500 g/ton of Na_2SiF_6 for 10 minutes, and floated with 250 g/ton of S-3903 after 10 minutes conditioning. At the end of the magnetic separation, the fluorite concentrate was upgraded to 79.66% CaF_2 , and the recovery to 45.45%.

The last experiment was made with composite ore ground to -48 mesh (-295 μm). By using 850 g/ton of S-3903 collector (as 350 g/ton, 350 g/ton, and 150 g/ton) barite flotation was applied at pH 7.9. Conditioning times for collector were 20 minutes at the beginning, and 10 minutes at the second and third steps. The grade of the barite concentrate was too low, therefore only the fluorite concentrate was upgraded by high intensity magnetic separation. The recovery of the fluorite concentrate was increased to 55.32%, when the grade was 79.81% CaF_2 (Figure 16).

The results of the concentration studies performed by the combination of flotation and magnetic separation techniques proved that the grade of the fluorite concentrate satisfied the metallurgical grade fluorite, whereas the grade of barite concentrate was too low.

Only metallurgical grade fluorite concentrates were obtained by the combination of flotation and magnetic separation techniques.

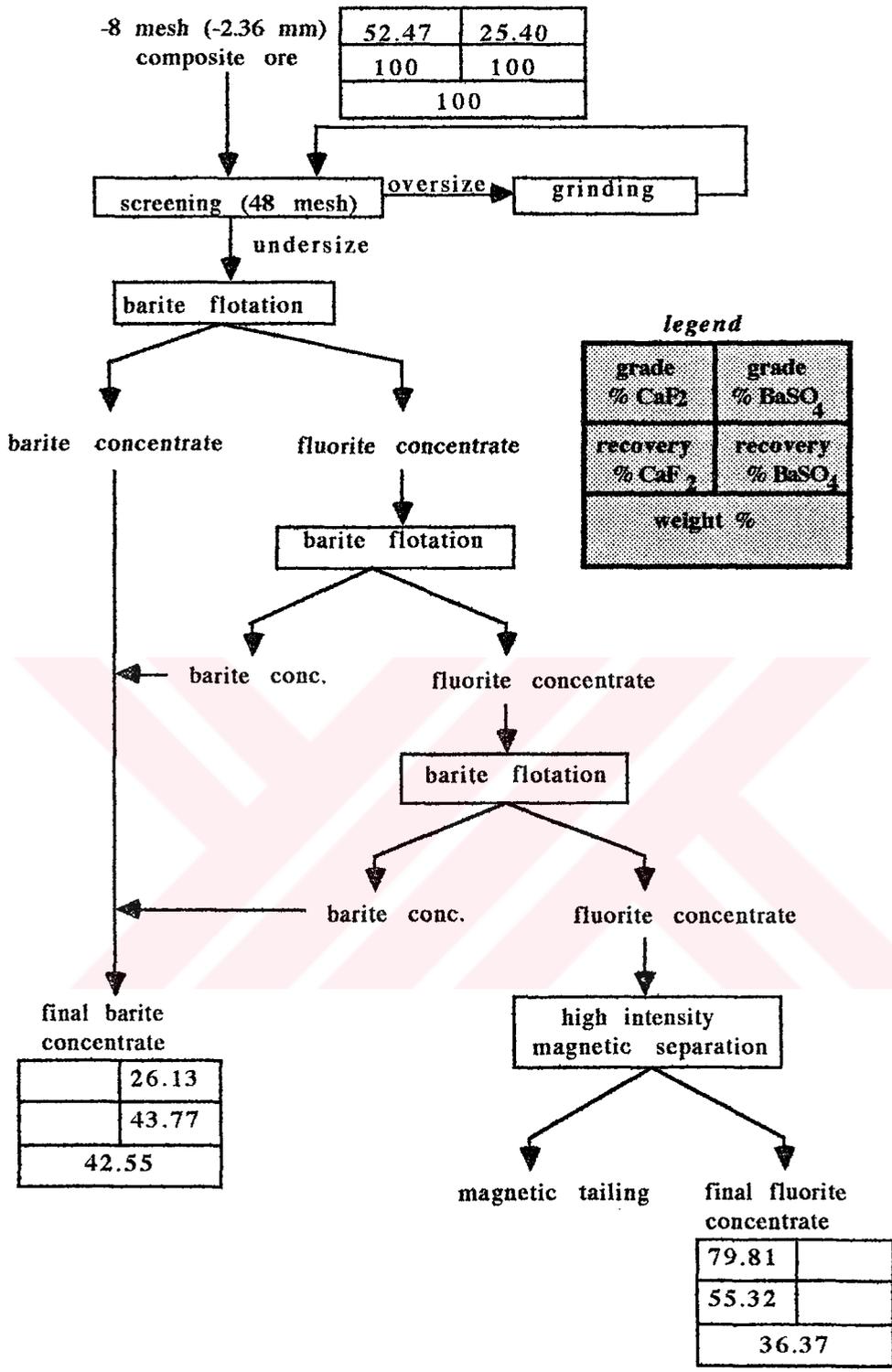


Figure 16. Concentration of Barite and Fluorite by the Combination of Flotation and High Intensity Magnetic Separation

The results of concentration studies can be summarized as follows:

Gravity concentration studies showed that, drilling mud grade barite and metallurgical grade fluorite concentrates can be obtained by tabling. According to the results of the flotation studies, in order to obtain more selective fluorite concentrates with higher recoveries, reverse flotation of fluorite is more successful than direct flotation. On the other hand, only metallurgical grade fluorite can be obtained by reverse flotation of fluorite. Therefore, it can be said that gravity concentration is necessary to obtain drilling mud grade barite concentrate.

In order to obtain higher grade fluorite concentrates with higher recoveries, the combination of gravity concentration and flotation was applied. Although the grade of fluorite concentrate was increased up to 75% CaF_2 , ceramic grade fluorite could not be obtained during this group of studies.

During the gravity concentration studies it was observed that, mica minerals (e.g. biotite) were concentrated with fluorite while iron minerals (e.g. hematite, limonite) were concentrated with barite. The removal of these impurities was necessary to increase the grades of both barite and fluorite concentrates. Therefore, concentration studies were performed by the combination of gravity concentration-flotation-magnetic separation. Improvement in grades of both barite and fluorite concentrates was observed during these studies. No. 2 ceramic grade fluorite, and barite suitable for chemical manufacturing were obtained.

Concentration studies including flotation followed by magnetic separation were also performed. Although the grade of fluorite concentrate was increased up to 82.58% CaF_2 , the grade of barite concentrates were still too low.

CHAPTER VI

CONCLUSION

1- It is possible to obtain barite concentrate suitable for chemical manufacturing and/or drilling mud additive from Eskişehir-Beylikahır complex ore.

2- It is also possible to obtain metallurgical grade and/or No.2 ceramic grade fluorite concentrate from Eskişehir-Beylikahır complex ore.

3- By gravity concentration, barite concentrate assaying 90.50% BaSO_4 with 25.97% recovery, and fluorite concentrate assaying 74.80% CaF_2 with 70.00% recovery were obtained.

4- Separation of slime before grinding was reduced recovery losses of barite and fluorite in gravity concentration.

5- Grinding of the composite ore to finer sizes than -48 mesh (295 micron), increases the amount of slime, and so the recovery losses of both barite and fluorite.

6- More selective fluorite concentrates were obtained with reverse flotation of fluorite.

7- A fluorite concentrate assaying 70.54% CaF_2 with 68.22% recovery was obtained by reverse flotation of fluorite, whereas the grade of the barite concentrate was very low.

8- Although the combination of gravity concentration and flotation was applied to increase fluorite grade and recovery, only 75.00% CaF₂ grade with 59.61% recovery was obtained.

9- High intensity magnetic separation is necessary to remove magnetic impurities such as biotite obtained with fluorite, and hematite obtained with barite in gravity concentration.

10- A fluorite concentrate assaying 92.18% CaF₂ with 45.42% recovery, and a barite concentrate assaying 90.00% BaSO₄ with 49.56% recovery were obtained by the combination of gravity concentration-flotation-magnetic separation.

11- As an alternative, by the concentration of +65 mesh and -65 mesh fractions (+208 and -208 micron) of the composite ore separately, another fluorite concentrate assaying 91.85% CaF₂ with 51.98% recovery, and another barite concentrate assaying 87.45% BaSO₄ with 49.61% recovery were obtained by the same combination of gravity concentration-flotation-magnetic separation.

12- Concentration studies including flotation followed by high intensity magnetic separation increased fluorite grade up to 82.58% CaF₂ with 39.77% recovery, whereas the grade of barite concentrate was again too low like the results of flotation studies.

13- Gravity concentration is necessary to obtain marketable barite concentrate.

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APPENDIX

APPENDIX A

FLOTATION REAGENTS

MIBC: methyl isobutyl carbinol, a synthetic alcohol frother (Shell Company).

A723: a refined fatty acid with a total fatty acid (RCOOM) content of 92% and a rosin acid content of roughly equal parts of oleic ($C_{17}H_{33}COOH$) and linoleic ($C_{17}H_{31}COOH$) acids (Cyanamid Company).

A845: anionic alkyl succinamate promoter developed to provide more selectivity than can be had with fatty acids (Cyanamid Company).

S-3903: a homologue of A845 (Cyanamid Company).

Na-oleate: an oleic acid salt ($C_{17}H_{33}COONa$) which is freely soluble in water.

Na_2SiO_3 : depressant for calcite and siliceous gangue.

Na_2SiF_6 : depressant for fluorite.

Na_2CO_3 and HCl: pH modifiers.