

Beneficiation of Rutile Ore by Combined Agglomeration and Flotation Methods

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ABSTRACT

Titanium known as a rare element is the most abundant sixth element in the earth crust. Titanium tend to be precious, due to its rare ore concentration and obtaining from metal ore. Most of ore is used TiO_2 (titanium oxide) form. Titanium oxide is known as white painting material. Apart from that it is also widely used in many fields such as cosmetic industry, linoleum (cerecloth), synthetic silk, white ink, colored glass, ceramic glaze, leather and cloth dyeing, welding rod construction and paper industry. TiO_2 is obtained from titanium ores, sulphate and chloride methods. The old sulphate method produces a lot of environmental pollution. On the other hand, Chloride method requires very high graded ores. As for titanium beneficiation methods, flotation, gravity beneficiation, magnetic separation and beneficiation via electrostatic separation methods are used. Rutile is the most important titanium mineral. It is considered that the most important titanium reserves in Turkey are in Manisa with 1.11% TiO_2 tenor and 1.272.000 ton, total reserves are 100 million ton with 0.5-1% TiO_2 tenor. Rutile samples used in this study were taken from region Manisa-Alasehir. Rutile samples with -106 μm grain size were subjected to agglomeration and flotation together with using different pH and reactives. According to the test results, the highest $TiO_2\%$ tenor was obtained with 11.90% value in pH: 4, the highest recovery was obtained with 79% value in pH: 7.

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KEYWORDS

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تخصيب خام روتيل (Rutile) بدمج طريقتي التغطية والتعويم

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المُستخلص

التيتانيوم هو العنصر النادر والسادس الأكثر وفرة على سطح الأرض ويعتبر من المعادن الثمينة، ويرجع ذلك إلى أنه خام عالي التركيز ونادر يتم الحصول عليه من خامات المعادن. يُستخدم في الحصول عليه خام TiO_2 المنشط (ثاني أكسيد التيتانيوم). وأكسيد التيتانيوم عبارة مادة بيضاء اللون تستخدم في طلاء المعادن، وفي العديد من الصناعات كمستحضرات التجميل، كريمات دهن البشرة cerecloth والحبر الصناعي، والحبر الأبيض والزجاج الملون والسيراميك المصقول، والجلود وصباغة الأقمشة، وفي لحام قضبان البناء وصناعة الورق. يتم الحصول على ثاني أكسيد التيتانيوم المنشط TiO_2 من خامات التيتانيوم بطرق الهدرجة والكبريتات sulphate and chloride. ينتج عن الأسلوب المتبع قديماً الكثير من الأملاح والكبريتات التي تسبب في التلوث البيئي. ومن ناحية أخرى يتطلب أسلوب متدرج كلوريد خامات عالية الجودة. أما بالنسبة للطرق الحديثة المستخدمة في تخصيب التيتانيوم فتجد التعويم وإثراء الجاذبية والفصل المغناطيسي والتخصيب عبر طرق الفصل الكهربائي. ويعتبر خام الروتيل Rutile هو المعان الأكثر أهمية في الحصول على التيتانيوم. يعتبر أن احتياطي التيتانيوم الأكثر أهمية في تركيا إذ يوجد منطقة مانيسا كخليط بنسبة 1.11% من ثاني أكسيد التيتانيو TiO_2 المحفز (المشع) في كل 1.272.000 طن، وإجمالي الاحتياطيات يبلغ حوالي 100 مليون طن ويوجد بنسبة تتراوح ما بين 0.5-1% TiO_2 من ثاني أكسيد التينوز. وفي هذه الدراسة تم أخذ عينات خام الروتيل المستخدمة من منطقة مانيسا. كما تم تعريض حبيبات خام الروتيل بحجم 106 μm ميكرون حجم الحبوب إلى التكتل وتعويم جنباً إلى جنب مع استخدام الرقم الهيدروجيني ومفاعلات مختلفة. وفقاً لنتائج الاختبار، تم الحصول على أعلى نسبة من ثاني أكسيد التينوز TiO_2 النشاط مع قيمة 11.90% في درجة pH: 4 كما تم الحصول على أعلى قيمة الانتعاش مع 79% في درجة pH: 7.

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الكلمات الدالة

تكتل، تعويم، معادن صناعية، التيتانيوم،
إثراء، مانيسا، تركيا

Introduction

Titanium is a light, strong, bright, corrosion-resistant and grayish transition metal. It is hard enough to scratch quartz on its metal form. Despite its superior metallic properties, it is used for most of the ore production as TiO_2 (titanium oxide) without being reduced to metal. Although titanium is known as a rare element, it is the sixth most found element in the earth's crust. But, since its ore concentrations are scarce and it is too difficult to produce titanium from the ore, it is a very precious metal. The most prominent minerals of titanium in commercial value are ilmenite (FeTiO_3) and rutile (TiO_2). Rutile contains 60% Ti, 40% O_2 and traces of iron; and ilmenite contains 31.6% of Ti, 36.8% of Fe and 31.6% of O_2 . Rutile ore contains approximately 95% of TiO_2 , meanwhile ilmenite ore contains around 40-60 % of TiO_2 , depending on the structural differences. Although valued rutile ore is very scarce in the wild commercially, ilmenite ore is quite abundant and spread out. Nearly all of rutile is obtained from beach sands and ilmenite is obtained from beach sands as well as ore deposits.

Abraham Gottlob Werner created the name rutile (Ludwig 1803), which rutil is originally known as "red schorl". The first description of "red schorl" is commonly attributed to Romé de l'Isle in 1783. used "red schorl" (rutile) for the description of the element titanium, which he named after the Titans of Greek mythology (Klaproth 1795). Note that William Gregor originally discovered titanium (which he named menackanite) in ilmenite in 1791 (Trengeve 1972). The name "rutile" is derived from the Latin rutilus because of the deep red colour observed in some specimens in transmitted light. Rutile can be translucent or opaque. Yellowish and brownish colours are also very common. A rarity is natural rutile with blue colour, which has been described so far as needle-like inclusions in garnet from ultrahigh-pressure metasedimentary rocks of the Greek Rhodope Massif (Mposkos and Kostopoulos 2001). In reflected light rutile with bluish colour has been reported from several meteorites (El Goresy 1971). The blue colour of meteoritic rutile may be due to a stoichiometric

deficiency of oxygen in the rutile structure (El Goresy 1971). Experiments on synthetic rutile have shown that blue colours occur in rutile samples grown or annealed under reducing conditions (Bromiley and Hilairret 2005). The colour of blue rutile is mainly due to intervalence charge transfer between Ti^{3+} and Ti^{4+} ions on adjacent interstitial and octahedral sites see (Bromiley and Hilairret, 2005). Rutile has a density of 4.23 g cm^{-3} , but can range up to 5.50 g cm^{-3} (Deer *et al.* 1992), and thus belongs to the heavy mineral suite, which are minerals with density $\geq 2.8 \text{ g cm}^{-3}$. Rutile is commonly diamagnetic (non-magnetic), and therefore, it can easily be separated from the paramagnetic (weakly-magnetic) and ferromagnetic (strongly-magnetic) heavy mineral fraction using the Frantz isodynamic separator (Buist 1963). However, rutile can also contain a high proportion of Fe making it magnetic, and hence it could remain in the magnetic heavy mineral fraction (Buist 1963, and Hassan 1994). Bramdeo and Dunlevey (2000) mentioned anomalous behaviour of detrital rutile (due to substitution of cations other than Ti^{4+} in the rutile crystal lattice) during industrial magnetic and electrostatic mineral separation, which can cause rutile loss. Recent studies show that Co-implanted rutile can become ferromagnetic (Akdogan *et al.* 2006). The melting point of pure rutile is around $1825\text{--}1830^\circ\text{C}$ (MacChesney and Muan 1959, and Deer *et al.* 1992). Note that synthetic rutile can be produced by heating a solution of TiCl_4 to 950°C or by heating anatase to above 730°C (Deer *et al.* 1992, and Guido 2010).

Titanium can be used as metal and its alloys, as well as oxide and its compounds: Metallic titanium has superior physical and chemical properties. Therefore, it is an irreplaceable metal in spacecraft, aircraft and missile construction. It is widely used in vehicle parts where high speed, vibration and high temperatures are operated on engine turbine wings and similar other overloaded vehicle parts. Its chemical resistance is its reason of usage in factories which produce corrosive chemical materials. Titanium oxide is known as white painting material. Apart from that it is also widely used in many fields such as cosmetic industry, linoleum (cercloth), synthetic silk, white

ink, colored glass, ceramic glaze, leather and cloth dyeing, welding rod construction and paper industry. Although it has so many usage fields, 60% of total produced titan oxide is consumed by paint industry. Titan chloride which is deriving from its other compounds is used to bleach to colors of cloth, tetra chloride is used in synthetic fog obtainment and titanium carbide is used as a corrosive.

Materials and Methods

(1) Materials

Beneficiation of Titanium Ores

Titanium is the ninth most abundant element of the Earth's continental crust. The most important titanium minerals are rutile (TiO_2), ilmenite (FeTiO_3) and titanite (CaTiSiO_5). Rutile is an accessory mineral in a variety of metamorphic and igneous rocks and occurs as a detrital mineral in clastic sediments. Although the main formula of rutile is (TiO_2), there are commonly several possible substitutions for titanium, for example, (Al, V, Cr, Fe, Zr, Nb, Sn, Sb, Hf, Ta, W, and U) (Graham and Morris 1973, Hassan 1994, Fett 1995, Murad *et al.* 1995, Smith and Perseil 1997, Rice *et al.* 1998, Zack *et al.* 2002, Bromiley and Hilaret 2005, Scott 2005, and Guido 2010).

Rutile minerals contained in alluvial deposits are conventionally concentrated by a combination of gravity, magnetic and electrostatic separation techniques. However, for hard rock rutile ores, the concentration circuits usually include flotation besides gravity and magnetic separation operations (Lynd and Lefond 1983). Very limited information on rutile flotation is available in the literature. studied the flotation of rutile crystals by unsaturated fatty acids (oleic, linoleic and linolenic acids). Rutile crystals could be floated in a wide pH range from 2 to 11 when the concentration of oleic acid was 10 -3 mole/liter (Purcell and Sun 1963). The pH range of floatability became narrower when the concentrations were reduced, or when the degree of unsaturation of the fatty acids increased. The floatability ranges seemed to converge to pH 4 to 5 studied the flotation of rutile minerals using a chelating agent, Nbenzoyl- N-phenyl-hydroxylamine (Marabini and Rinelli 1983). Good

rutile flotation was observed between pH 2 and 4. The reagent was selective against hematite below pH 2. Both of the cited studies were performed using Hallimond tube flotation tests. Developed a synthetic copolymer, 3,4-(methylenedioxy) benzyl acrylate/acrylic acid, as selective flocculant for fine rutile and other titanium minerals (Bertini *et al.* 1991). It was reported a process in which rutile was recovered from a porphyry copper flotation tailings (Llewellyn and Sullivan 1980). After a bulk flotation that removed sulphides and carbonates, the rutile was floated by a petroleum sulphonate in an acid circuit. It was studied the flotation of a rutile ore containing rutile and chlorite (Ma 1989). He observed that at pH 8 to 9, by using sodium hydroxamate as a rutile collector, sodium hexametaphosphate and carboxymethyl cellulose as gangue depressants, a rutile rougher concentrate assaying 42% TiO_2 was floated at 72% recovery. The rougher concentrate was then acid leached and cleaned. The cleaned concentrate was roasted to remove sulphur. The final concentrate assayed 80.4% TiO_2 and the overall recovery was 57.4%. It was developed a flotation reagent scheme for the rutile ore of Zaoyang Rutile Mine, China (Cui *et al.* 1986). They used sodium fluorosilicate (Na_2SiF_6) as a gangue depressant, benzyl arsenic acid as a rutile collector. By using sulphuric acid to adjust pH to 4.5, they floated a rutile concentrate assaying 84.5% TiO_2 from a tabling concentrate. The recovery of the flotation process was 86.4%. They found that the fatty acids type collectors were not effective. The procedure and the reagent scheme were employed in the Zaoyang Rutile Mine. However, two problems soon arose. Benzyl arsenic acid was a toxic reagent and caused environmental problems. Secondly, the restrictions on benzyl arsenic acid production resulted in a high reagent cost and the process became marginally economical. A study was carried out with the objective of finding a substitute to replace the benzyl arsenic acid used in the Zaoyang Rutile Mine (Liu and Peng 1999).

Titanium (TiO_2) is a white pigment used in paints, paper, plastics, cosmetics and coatings. It was used for a wide range of applications due to its higher opacity and covering power. There

are two commercial methods of TiO_2 production, the chloride and the sulphate process. In the chloride process, titanium mineral is converted into TiCl_4 which is subsequently oxidized at high temperatures. In the sulphate process, the ore is converted into sulphate solution and then thermally hydrolysed to hydrous titanium. The latter is calcined to produce the pigment (Braun *et al.* 1992, Nielsen and Chang 1996, and Xue *et al.* 2009). According to a commercially viable process has to be environmentally benign, to generate a minimum waste, be able to use all grades of ores and be economically favourable (Pong *et al.* 1995). The above processes are, either environmentally unfriendly, costly, generate high levels of waste or recycle, or are unable to process low-grade ores, as well as, ores such as anatase, sphene, and perovskite (Bulatovic and Wislouszyl 1999, Cole 2001, Nielsen and Chang 1996, Van Dyk *et al.* 2004, and Yuan *et al.* 2005).

Generally low-grade titaniferous ores are submitted to slagging process. The slagging process however faces uncertain future due to its higher energy consumption and green house gases emission. Additionally, slagging is unable to treat radioactive ores, since the radionuclides remain in the solid solution during slagging process. With increasingly stringent environmental policies on radionuclides content, further treatment has to be conducted to reduce it. This will result in additional production costs (Nielsen and Chang 1996, Habashi 1997, Doan 2003, Lahiri *et al.* 2006, Lahiri and Jha 2007, and Jha *et al.* 2007). There is a need in converting the existing methods to ecologically and environmentally friendly as well as cost effective methods. This study presents a novel process of titania recovery from low-grade ores. The process entails roasting of titanium ore with alkaline metal salt. The roasted product is hydrolysed with water, acid and subsequently reacted with sulphuric acid. Alternatively the hydrolysed product can be used as feedstock in chloride process (Arao *et al.* 2011).

(2) Methods

Agglomeration and Flotation Methods with Beneficiation

(1) Agglomeration Method

Agglomeration method is used in various field of industry. Fine grained materials are turned into large agglomerates and an ease of transportation and material property for the following process is obtained. Agglomeration is also used in obtainment of the scarce in spite of commercially high valued minerals. This method brings hydrophobic particles together by using a second liquid adsorbing to hydrophobic particles in the suspension and not mixing with water. During the agglomeration, solids scattered across the liquid suspension as fine grain are processed with a second liquid that preferably moistens the solids and does not mix with the first liquid. This second liquid is called the bridge liquid. When the suspension is mixed, bridge liquid is distributed to the surfaces of the solids. As a result of collision of the grain, bonding strength among the colliding grains is adjusted by the bridge liquid's inner surface. Heavy oils are mainly used as collecting liquid. Surface conditioning is obtained by mixing systems that apply slow, but high friction strength that forces mineral grains into oil phase. Provided that the suspension is formed of natural grain, oils and grains can directly get together to form agglomerates and if the suspension is formed of hydrophilic grains, it is necessary for the grain surfaces to form hydrophobics via collectors and then oils and agglomerates must be formed (Bilgin 2002).

(2) Flotation Method

Flotation means to float. In ore preparation, flotation is a beneficiation method that fine milled ores are floated and enriched on foam, based on physicochemical, surface chemistry and colloids. Flotation process is a very complex beneficiation method that is applied to minerals which are possible to be separated into very fine grain sizes, which have the widest usage field in mining industry today. It is the most widespread beneficiation method worldwide today. Flotation method caused the mining industry to develop because it made possible to process low graded or complex structured ore deposits that were previously deemed

worthless due to the inability of beneficiation via gravity methods. Different minerals within the pulp, which is a solid material (fine milled ore) and water mixture, exhibit different outer surface properties. Some of these minerals have hydrophobic and some of them have hydrophilic properties. Hydrophobic minerals are hardly heated; on the other hand hydrophilic minerals outer surfaces are more easily moistened. Different behaviors of these minerals in the flotation environment increase to be applied reactive combinations and therefore hydrophobic minerals attach to the artificially created air bubbles and gather at the surface. This mechanically ordered mineral group is called concentrate. The remaining hydrophilic mineral group is defined as tailing. Physical parameters active in the flotation method are pH setting, grain size, pulp properties, pulp density and pulp temperature. Chemical parameters are phases, zeta potential, surface properties and chemical reactives (Bilgin 2002).

Results

In this study, the rutile sample taken from the rock from Manisa-Azitepe-Alasehir is enriched with agglomeration and flotation methods and researched and evaluated for the results accordingly. Rutile samples used in this study are taken from Manisa, Alasehir region. Taken samples are broken in the primary and secondary crushers and reduced under 3.00 mm. After that, the obtained material is subjected to roll crusher and with a closed circuit, all of the material is reduced under -1.00 mm and assessed by sieve and microscopic analyses. Sieve analysis which is under-sieve curve is shown in Figure 1.

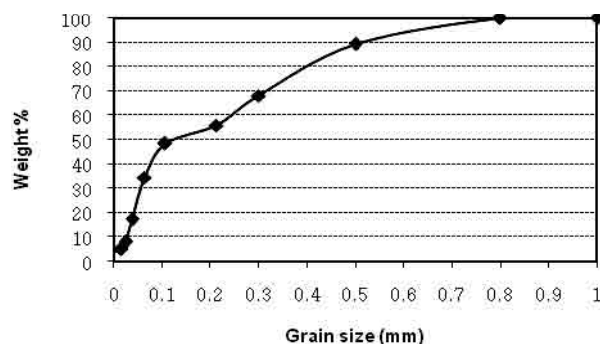


Figure 1: Rutile Sample -1 mm under-sieve curve. The microscopic analysis results of the rutile sample are given below:

- 1.000-0.800 mm: No standalone liberated metals are found within the relatively huge material.
- 0.800-0.500 mm: Grain size is still huge, liberated periods are in scarce amounts.
- 0.500-0.300 mm: Grains are recently starting to separate, additionally small amounts of liberated grains made of amphibole and plagioclase.
- 0.300-0.212 mm: Hornblendes and feldspat are separated in this point and standalone amphiboles and garnets are found. Biotites are transferred into plate phase.
- 0.212-0.106 mm: Rutile minerals are still in compound shape, additionally rutiles within amphiboles are found in this interim.
- 0.106-0.063 mm: Free rutile amount is observed around 3-4%.
- 0.063-0.038 mm: Free rutile amount is higher compared to the previous stage.

In Table 1 illustrates the Rutile sample chemical analysis. Accordingly, TiO_2 grade is found in the amounts of 5.09%.

Table 1: Rutil Sample Chemical Analyses Results

SiO_2	30.45%
CaO	12.46%
MgO	8.75%
Fe_2O_3	9.50%
TiO_2	5.09%
Others	23.40%

According to rutiles sample microscopic observation results, liberalization starts in 0.106 mm in size, agglomeration and flotation beneficiation experiments are performed in this size and below (figure 2).

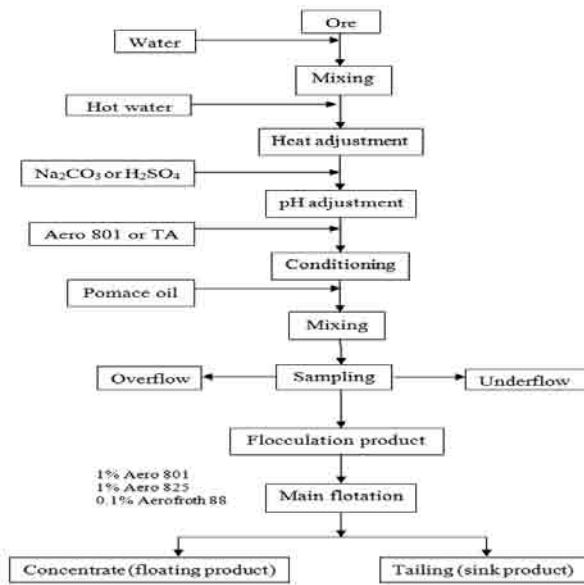


Figure 2: Rutile Sample Agglomeration and Flotation Flow Chart.

Table 2: 106 μm Grain Sized Rutile Sample Agglomeration Experiments Conditions

Agglomeration Conditions						
Experiment No	pH	Heat (°C)	Conditioning Speed (cyc/min)	Conditioning & Mixing (min.)	Settling (min.)	Reactives
1	Neutral	40	1500	5	3-5	1% Aero 801 (600 g/t), pomace oil (30 kg/t), hot water
2	9.5	40	1500	5	3-5	1% Aero 801 (600 g/t), pomace oil (30 kg/t), Na_2CO_3 , hot water
3	4	40	1500	5	3-5	1% Aero 801 (600 g/t), pomace oil (30 kg/t), 15% H_2SO_4 , hot water
4	Neutral	40	1500	5	3-5	1% TA (600 g/t), pomace oil (30 kg/t), hot water
5	10	40	1500	5	3-5	1% TA (600 g/t), pomace oil (30 kg/t), Na_2CO_3 , hot water
6	4	40	1500	5	3-5	1% TA (600 g/t), pomace oil (30 kg/t), H_2SO_4 , hot water

Agglomeration-Flotation Method and the Assessment of the Experiment Results

Rutile sample, originating from Turkey-Manisa-Alasehir region as a Titanium mineral has been reduced to -106 μm (for E.1, E.2, E.3, E.4, E.5, E.6 experiments) by required crushers and ball mills and packed in bags of 500 g each. Flotation-agglomeration beneficiation method has been performed as six different experiments in this grain size (with the usage of different pH and different anionic and cationic reactives). Six performed experiments (Agglomeration & Flotation Experiments) are actualized according to the variable reactive and pH values are shown in Table 2 and table 3 and over the general flow chart in Figure 2.

Table 3: 106 μm Grain Sized Rutile Sample Flotation Experiments Conditions

Flotation conditions				
Experiment No	Conditioning Speed (cyc/min)	Conditioning & Mixing (min.)	Foam Taking Time (min.)	Reactives
1	1500	5	15-20	1% Aero 801 (400 g/t), 1% Aero 825 (400 g/t), 1% Aero Froth 88 (100 g/t)
2	1500	5	15-20	
3	1500	5	15-20	
4	1500	5	15-20	
5	1500	5	15-20	
6	1500	5	15-20	

Discussions

(I) Experiment of Products (Experiment No.1)

(1.1) Product that Floats in Agglomeration

Concentrate and tailing are equally distributed gravimetrically. Flocculation and subsequently green and white rock minerals in agglomeration position are dominant in the concentrate. Heavy minerals and amphiboles in approximately 3-5% are stuck closed within those flocculed grains and transferred to this product. The possibility to remove this with a proper presser must be researched. Particularly fine grains are (aforementioned rock minerals) are prone agglomeration after flocculation. When it is bated and analyzed, agglomeration structure is disassembled and black colored amphiboles, garnets and rutile in low amounts are observed in 1-2%.

(1.2) Product that Sinks in Agglomeration

It is observed that it is generally formed of large green and white rock minerals and heavy minerals are observed in between, particularly rutile. Agglomeration structure is not observed. Particularly large size grains are observed. When it is bated and analyzed, amphibole and rutile amount is increased.

(1.3) Result

As selective flocculation and consecutively, by selective agglomeration, particularly fine grained white and green colored rock minerals shift into another phase and with the flocculation applied

(reverse flotation) they are floated and taken. The sinking part is usually the large grained, black colored amphiboles, ilmenite and white-green rock minerals and rutile. Flotation and connectively agglomeration are not observed in main bulks, the agglomerates which were to float because of flotation, could not float due to limited flotation time. These agglomerates are comprised of fine grained white and green grains. With the reactive type, presser and amount based optimization of experiment conditions; it is observed that it is possible to take grain size with this selective flotation-agglomeration reverse flotation method and pre-concentrate rutile of the sinking part. According to the experiment results, TiO_2 percentage and efficiency percentage graph of rutile sample agglomeration-flotation experiment products are shown in Figure 3.

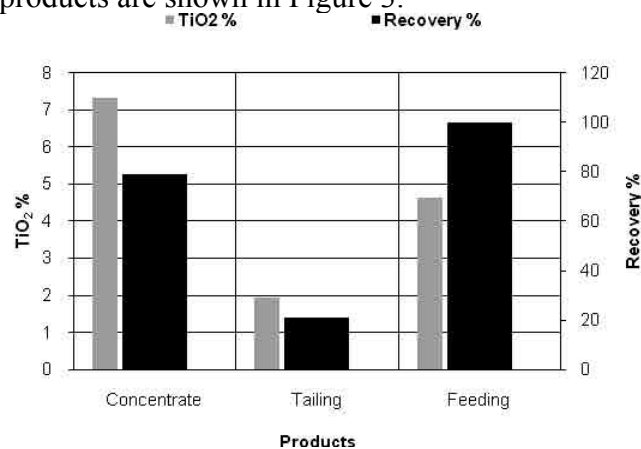


Figure 3: Experiment No 1 Agglomeration Flotation Results.

(2) Experiment of Products (Experiment No. 2)

(2.1) Product that Floats in Agglomeration

The taking of fine grained white colored, of which the mineral compounds are selectively flocculed, with selective differential flotation experiments these micro sized mineral grains can be flocculed (means the forming of agglomerate in micro size) and floated, must be accepted as the first phase. However, it is suggested that consecutive experiments to this experiment cation must be tested with active reactivities in pH: 10 and flocculation event to be observed by microscope and flotation stage must be proceeded accordingly.

(2.2) Product that Sinks in Agglomeration

Large sized green colored amphibole grains and garnet and rutile is not flocculed and devoid of slime. Additionally metallic iron and ilmenite in small amounts are observed.

(2.3) Result

When the ore is milled to smaller sizes, it is possible to force the white and green components left in the large sized part to be subjected to selective flocculation and transfer to the fine grained part. Therefore it is possible to obtain a rutile enriched product in the large size. And this product must be subjected to rutile flotation application. With this aspect, it is possible to define it as reverse agglomeration method. It is suggested that anion, cation instead of active reactive Aero801 and amines of active reactivities can be used to perform the experiment and result to be observed and then proceeded to the flotation application.

(2.4) Flotation Concentrate

On the contrary of the previous experiment's concentrate, larger size grained, particularly white and green colored amphiboles and heavy minerals have been agglomerated. It is observed that pH has a positive effect in agglomerating the large grain, in terms of selectivity it had a negative effect and amphiboles have also come with it. Accordingly, it has come gravimetrically 65% to the concentrate. When the concentrate has been bated and analyzed, heavy minerals have transferred to agglomerates without exhibiting selectivity on the contrary of this product of the previous experiment.

(2.5) Flotation Tailing

No agglomeration formation has been observed.

Amphiboles and green pyroxenes are dominant on large grains. When it is bated and analyzed, it is observed that rutile has been subjected to pre concentration in this product. There are no ilmenites or pyrites as heavy minerals next to rutile.

(2.6) Result

It is observed that fine grained amphiboles, pyroxenes and white rock minerals form together agglomerate. It is also detected that rutile is concentrated in the sinking part. According to the results of this experiment, it is proper that serial experiments must be performed in different pH, for example from 8 to 11-12. Therefore, the agglomeration conditions of both green and black amphiboles must be researched. The fact that the experiment concentrate is gravimetrically high, numerically proves this notion. According to the experiment results, TiO_2 percentage and efficiency percentage graph of rutile sample agglomeration-flotation experiment products are shown in Figure 4.

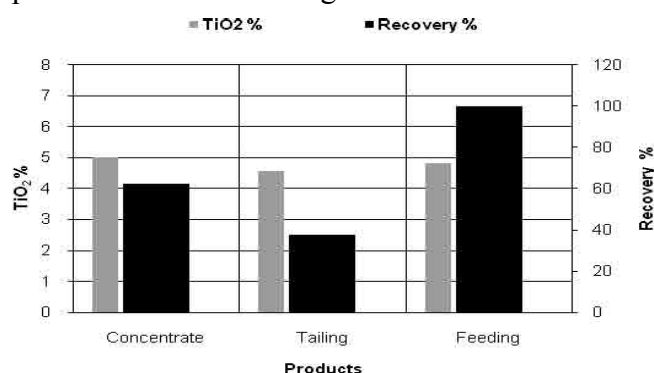


Figure 4: Experiment No.2 Agglomeration Flotation Results.

(3) Experiment of Products (Experiment No.3)

(3.1) Product that Floats in Agglomeration

Flocculation ratio and flocculed amount is low and not selective. But large sized garnet and rutile has also arrived to this part.

(3.2) Product that Sinks in Agglomeration

There is a loose flocculation notion. Quartz and plagioclase rock minerals initially exhibit a loose flocculation and garnet grains are locked inside. In fine grains (quartz and plagioclase), flocculation is observed but in garnet and rutile it is not observed. The layered structure of mica is not suitable for flocculation. Amphiboles, garnet and rutile have remained in large grain and were not subjected to flocculation due to their solidness.

(3.3) Result

It is suggested that the raw ore is minimized to very thin proportions, possibly under 40 μm and the experiment to be repeated.

(3.4) Flotation Concentrate

Gravimetrically, green rock minerals and amphibols in small amounts are in relative amounts, in neutral environment and according to pH: 10, come with rutile agglomerates. When they are bated and analyzed, rutile and ilmenite and other heavy minerals are suitable to float with their hydrophobic properties in this pH and they have come to the concentrate with Aero801 via floating.

(3.5) Flotation Tailing

It is 68.9% gravimetrically, generally formed of large sized amphibol-pyroxenes and biotites and 5% of it are comprised of agglomerates that were supposed to float but escaped as tailing. When it is bated and analyzed rutile and heavy minerals are in very scarce numbers, nearly absently, remained in this product and aforementioned selective flocculation, agglomeration and direct flotation applications have been performed on titan minerals (rutile-ilmenite) and floated on foam and concentrated.

(3.6) Result

It is observed that pH is an important factor in rutile concentration and is flocculed in acidic environment with fine grained green rock minerals and provides a pre concentrate by microscopic observations quantitatively. However, since it is known by literature data that rutile floats more efficiently in pH 2.5-3 due to zeta potential, it is suggested that this experiment should be repeated in at least pH 2.5-3 levels. However, a second experiment is suggested to be performed for raw ore minimized to smaller size as -63 μm . According to the experiment results, TiO_2 percentage and efficiency percentage graph of rutile sample agglomeration-flotation experiment products are shown in Figure 5.

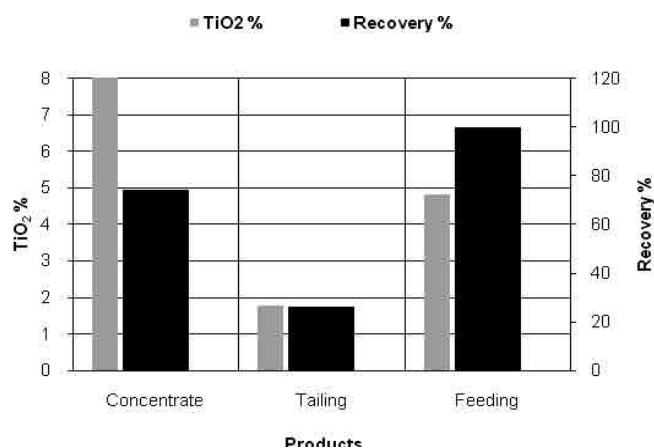


Figure 5: Experiment No.3 Agglomeration Flotation Results

(4) Experiment of products (Experiment No.4)

(4.1) Product that Floats in Agglomeration

A large chained selective flocculation is observed. When it is bated and analyzed, it is observed that large grained amphibole type rock minerals, rutile and mica are not subjected to flocculation.

(4.2) Product that Sinks in Agglomeration

Selective flocculation is observed in fine grained quartz and plagioclase and selective flocculation is not observed in other large grained minerals.

(4.3) Result

In neutral and alkaline environment positive flocculation has been observed in fine grained quartz and plagioclase and no flocculation has been observed in large grains (plagioclase and quartz) and other rock minerals (amphibole, garnet, rutile).

(4.4) Flotation Concentrate

Flocculation is comprised of fine grained green colored gang minerals. However it was not so selective. When it was bated and analyzed, it was observed that it includes rutile and heavy minerals with it.

(4.5) Flotation Tailing

Gravimetrically it is over 2% and generally comprised of large grained white and green colored rock minerals and dark colored amphiboles and micas. Flocculation and agglomeration events are not observed. Only in 1% amount the micro agglomerates that were supposed to be concentrated are left in the tailing. When it is bated and analyzed, only some of the rutile minerals are left in this fraction and no other heavy minerals are observed.

(4.6) Result

It is suggested that agglomeration is provided with TA-pomace oil and it should be floated with TA. According to the experiment results, TiO_2 percentage and efficiency percentage graph of rutile sample agglomeration-flotation experiment products are shown in Figure 6.

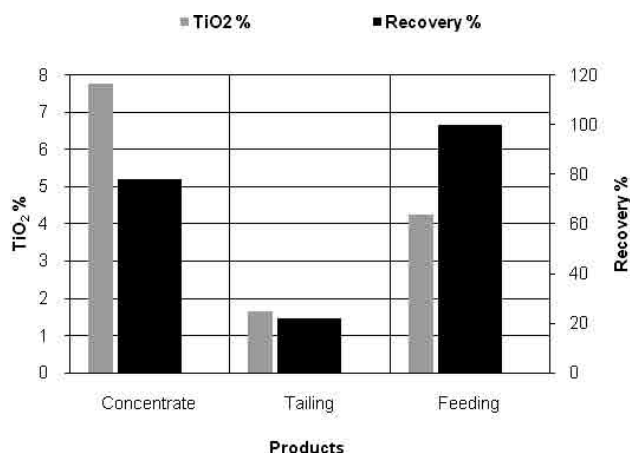


Figure 6: Experiment No. 4 Agglomeration Flotation Results.

(5) Experiment of Products (Experiment No.5)

(5.1) Product that Floats in Agglomeration

White, fine grained quartz and plagioclase form partially global, partially long chained flocculation viewed selective agglomerates. It is observed in pH: 10 that a more efficient flocculation on the contrary of Aero801 used flocculation notion. However in smaller sizes for example on 60 μm and 40 μm sized samples, these experiment conditions must be repeated and observed, and flotation experiments must be performed both this experiment and flocculation in smaller sizes.

(5.2) Product that Sinks in Agglomeration

Flocculation is very limited in large grains.

(5.3) Result

In pH environment in which used TA, flocculation (in quartz-plagioclase) is observed in larger, partially global and more selectively flocculations.

(5.4) Flotation Concentrate

When it is bated and analyzed, some of the heavy minerals have transferred to this product. It cannot be stated the selectivity is achieved. The reason for this is the usage of TA-Aerofroth series. It is suggested that this experiment is repeated with the usage of TA in agglomeration and flotation stages.

(5.5) Flotation Tailing

Non-agglomerated amphiboles and large grained pyroxene minerals and heavy minerals have remained. According to experiment results, it is observed that selectivity is provided, subjected to TA used agglomeration. The reason of rutile leaking into floating concentrate is the usage of Aero825, a selective collector. Therefore, it is suggested that pH: 10 agglomeration and flotation stages must be repeated, directed to the usage of TA with the pomace oil only.

(5.6) Result

Experiment must be repeated with TA usage. According to the experiment results, TiO_2 percentage and efficiency percentage graph of rutile sample agglomeration-flotation experiment products are shown in Figure 7.

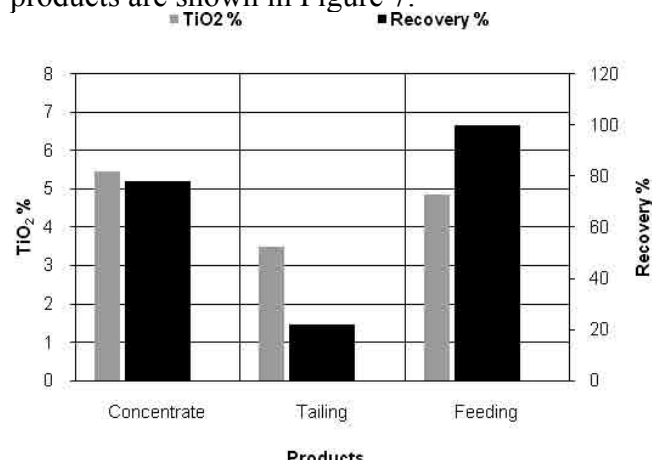


Figure 7: Experiment No. 5 Agglomeration Flotation Results.

(6) Experiment of Products (Experiment No. 6)

(6.1) Product that Floats in Agglomeration

A fine grain and very little flocculation (quartz and plagioclase) is observed.

(6.2) Product that Sinks in Agglomeration

No flocculation is observed.

(6.3) Result

No large grained flocculation is observed. In TA used environments between neutral and alkaline (pH: 10), relatively realization of quartz and plagioclase's selective agglomeration flotation is actualized. Particularly the fact that plagioclase have a lengthy structure prevents flocculation in large grains. Therefore, an agglomeration test must be performed in ore that is milled to 60 μm and 40 μm sizes and must be floated with foaming agents.

Agglomeration and subsequent flotation stage products must be analyzed in microscope.

(6.4) Flotation Concentrate

A strong flotation and agglomeration notion is observed. Some of the heavy minerals are in ilmenite, rutile concentrate.

(6.5) Flotation Tailing

A concentration of amphiboles and heavy minerals is observed in the tailing.

(6.6) Result

The usage of Aero825 in TA used agglomeration and flotation (in different pHs) application's flotation stage have prevented the selective gain of the gang in a rutile base. Therefore, it is suggested that the last three experiments are to be performed without the usage of Aero825 and with the usage of TA in both agglomeration and flotation stages, even this experiment should be performed in pH: 2.5 and added to the experiment series. According to the experiment results, TiO_2 percentage and Efficiency percentage graph of rutile sample agglomeration-flotation experiment products are shown in Figure 8.

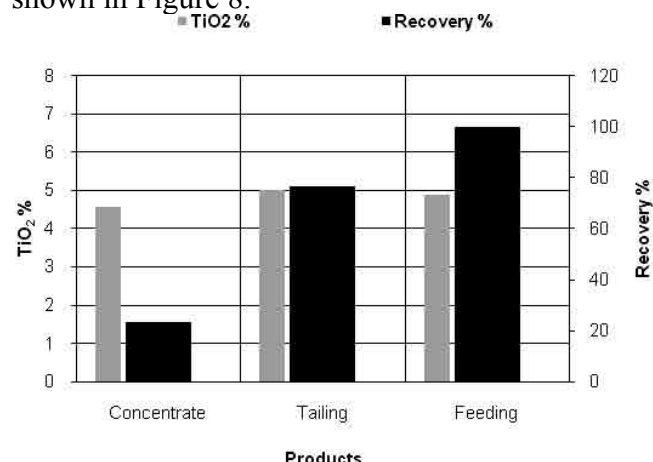


Figure 8: Experiment No. 6 Agglomeration Flotation Results.

Conclusions

The reactive type and its amounts and the pH values of the sample, which was mentioned at the experimental stage of the study as an active parameter during the applied both agglomeration and consecutive flotation stages, are researched. These parameters are detected in forefront 6 experiments in agglomeration-flotation combined methods. Rutile sample taken from the field

are minimized to -1 mm size after primary and secondary crushing operation and subjected to sieve analysis. At this stage, 89.3% of the ore is reduced to -0.8 mm and approximately 35% of it is reduced to 0.106 mm and 8.3% of it is reduced to 38 μm . With this grain distribution, it is concluded that ore is not a friable ore and crushing and milling expenses would be high. Additionally, it is also detected that the sieve analysis fractions' titan analysis results change in a small grade between 4.15% and 5.92% TiO_2 . It is also concluded that the TiO_2 percentage does not change dramatically according to grain interim show that the minerals that form this size of an ore cannot be enriched with a classification according to structural properties.

According to chemical analysis, the raw ore includes a 5.09% of TiO_2 . According to chemical analysis results, since it is predicted the ore can be technically liberated under 106 μm , an agglomeration-flotation methods combination of this size must be preferred. It is detected in this research that, during the 6 agglomeration-flotation stages to defined the proper pH grade and proper reactive type, in the experiment 1-2-3 as pH 7, 9.5, 10 and experiment 4's flotation tests, the most suitable pH in terms of grade and efficiency is pH: 4. Experiment, in agglomeration in which the Aero801 and pomace oil is used and consecutively in the experiment in which Aero801 and Aero825 is used as collector and Aero Froth 88 as foaming agent, a concentrate of 30% gravimetrical ratio, 11.9% of TiO_2 grade and approximately 74% of TiO_2 efficiency is obtained. In the same reactive conditions however, the concentrate of 50%, could not exceed the value of 7.3% in TiO_2 grade and approximately 79% in TiO_2 efficiency, in pH: 7. As a measure of pH: 7 against corrosion, low TiO_2 grade presents an important alternative with its high efficiency.

In the experiments 4, 5 and 6 consecutive to the agglomeration stage in which the TA and pomace oil is used in cationic collectors in pH 7, 10 and 4, again after a flotation stage in which the Aero801 and Aero825, which were used as a collector in the previous three experiments, are used as a collector and Aerofroth 88 is used as a foaming agent, the concentrate in the most suitable experiment is

obtained in approximately 43% gravimetrically, meanwhile TiO_2 grade is obtained in 7.76% and TiO_2 efficiency is achieved in 78% in pH: 7 value.

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