

QUARTZ BLEACHING BY OXALIC ACID: RELATIONSHIP BETWEEN REJECTION RATE OF IMPURITIES AND COLOR RESPONSE

M.M.A Mohammed ^{1,*}, T. Güler ¹, E. Polat ¹, N. Çetin ², Ü. Kuşcu ²

¹*Muğla Sıtkı Koçman University, Mining Engineering Department, Muğla, Turkey*

(*Corresponding author: mumohammed@mu.edu.tr)

²*Mikroman Mining Company, Hisarardı, Yatağan, Muğla, Turkey*

ABSTRACT

Quartz beneficiation has been applied to meet market requirements by physical and/or chemical methods. Chemical beneficiation has long been investigated by inorganic (e.g. sulfuric acid) and organic (e.g. oxalic acid) acids. Oxalic acid bleaching of quartz ore has taken great interest. This work was conducted to investigate the relationship between metal (Fe, Al, Mg) rejection rates and color responses of bleached quartz ore. Bleaching tests were conducted in agitated pulp condition at different oxalic acid concentrations (0.01M, 0.04M, 0.1M and 0.4M) and temperatures (80°C, 90°C and 95°C) for 90 min. Efficiency of process was measured by colorimetric analysis applied on bleached quartz and chemical analysis (ICP-MS) applied on metal loaded leach liquor. Experimental results revealed that mineralogical composition of ore affected the oxalic acid bleaching of quartz ore. Whiteness could considerably be increased, and yellowness was decreased by manipulating the leaching temperature and acid concentration. But, proportional improvement in the redness could not be achieved possible due to presence of insufficiently leached free dark colored particles in addition to the necessity to apply oxidizing potential in strongly acid environment.

Keywords: Oxalic acid, bleaching, metal ion, color response, temperature

INTRODUCTION

Demand on quartz ore has always been high due to the variety of industrial fields where it is involved in. Quartz is associated with other dark color minerals in the earth crust that decrease its purity such as hematite, biotite, rutile, titanite and ilmenite [Yan et al, 1987]. These minerals are separated from the ore using different physical and chemical methods although biological method has been proved to be effective as well (Váradyová et al., 2003; Sarvamangala & Natarajan, 2011). Physically, the concentration of quartz is obtained by using sorting, magnetic separation and in some cases flotation (Al-Maghrabi, 2004; Dehler, 2006; Mowla et al.pany, 2008; Wang et al, 2014). The level of purity obtained by physical methods does not rise up to the level needed in the production of advanced technological products like solar panel and electronic batteries. This is achieved by chemical methods (leaching) by dissolving the coloring impurity minerals by the aid of various chemicals (Ubal dini et al, 1996).

The brightness of quartz ore, which is a measure of purity, is defined by color measures that can be determined by CIELAB color index (L, a, b) using a colorimeter. The “L” scale interprets the degree of whiteness in a range from 0 for pure black to 100 for diffuse white. Positive value for scale “a” represents red color while negative value is the measure of greenness. The scale “b” show yellowness for the positive value (+b) and blueness for negative (-b) (Field, 2004; Green, 1999).

Researches have been made on the chemical purification of quartz using different inorganic acids like phosphoric acid, sulfuric acid and hydrochloric acid, and organic acids (Banza et al, 2005;

Ubaladini et al 1996; Vegliò et al, 1996; Zhang et al, 2012). Among the several organic acids, oxalic acid ($\text{H}_2\text{C}_2\text{O}_4$) is one of the most widely used in the dissolution of iron impurities from quartz ore. This acid dissolves iron oxides both by non-reductive and reductive pathways. The dissolving of iron in oxalic acid results bivalent and trivalent complex iron ions $[\text{Fe}^{2+}(\text{C}_2\text{O}_4)_2]^{2-}$ and $[\text{Fe}^{3+}(\text{C}_2\text{O}_4)_3]^{3-}$. Free Fe^{2+} ion can be identified only in high acid solutions, while free Fe^{3+} ion is not likely to build-up in oxalic acid solutions. In the pH range 1-2, $[\text{Fe}^{3+}(\text{C}_2\text{O}_4)_2]^-$ and $[\text{Fe}^{3+}\text{C}_2\text{O}_4]^{2-}$ ions are stable, while at pH values less than 1, the $[\text{Fe}^{3+}\text{HC}_2\text{O}_4]^{2+}$ is the only complex ion existing in leach liquor (Cornell et al, 1987; Litter et al, 1988; Panias et al., 1996; Torres et al, 1989). The dissolution of iron was reported to be changed by the change in the heat and acidity in the reactor (Lee et al, 2006; Panias et al., 1996). De Endredy (1965) declared that ultraviolet light accelerated the reaction.

Whitening is the characteristic measure for the application arias of quartz ore. This study was performed to determine the relationship between color index and the rejection rates of Fe, Al and Mg by oxalic acid leaching. Effects of leaching temperature and acid concentration on the bleaching of quartz were clarified.

MATERIALS AND METHODS

Quartz ore sample (-300 μm) was provided by Mikroman company located in Yatağan region in Muğla, Turkey. Ore sample mineralogical characterization was performed by XRD, SEM and optical microscopy study. Characterization study revealed that main phase was quartz together with hematite, magnetite, albite, mica, ilmenite and rutile as trace impurities (Güler, 2015). The L, a and b values of the sample were determined as 80.02, 4.28 and 17.31, respectively. Leaching tests were performed by high purity analytical grade of oxalic acid ($\text{H}_2\text{C}_2\text{O}_4$ - 99%, Merck) in distilled water. A glass leaching reactor was constructed, in which teflon coated impeller and a thermometer were placed. Agitation was applied at 400 rpm using a mechanical stirrer (M-TOPS MS-3020D). Reactor was closed to the atmosphere by isolating materials. Reactor temperature was controlled by using a hot plate.

The leaching process was conducted at 60 % solid rate. Oxalic acid leaching was applied at different molarities (0.01 M, 0.04 M, 0.1 M and 0.4 M) at constant temperature adjusted to 80°C. Bleaching tests were also conducted at 90°C and 95°C adjusting the acid concentration to 0.04 M. All testes were set for 90 min. At the end of bleaching process, sample was taken from leach liquor for chemical analyses, which was determined by inductively coupled plasma mass spectrometry (ICP-MS). The material is then washed and the dried in drying furnace (Memmert UNB400) at 105°C. Color analysis was performed on dried sample using a colorimeter (CNP Spec CS-10) to measure the L, a and b values.

RESULTS AND DISCUSSIONS

The bleaching of quartz was performed at different oxalic acid concentrations and temperatures. Figure 1 represent the change in the rejection rates of Fe, Al and Mg by increasing the acid concentration. Sharp increase was observed up to 0.1 M acid concentration, above which gradual increase continued for the cases of Al and Mg. On the other hand, equilibrium was reached for Fe at the cited concentration. According to Panias et al (1996), types of complex ions are dependent on acid concentration, and therefore pH of the system: trivalent complex iron ion - $[\text{Fe}^{3+}\text{C}_2\text{O}_4]^{2-}$ converts at first into $[\text{Fe}^{3+}(\text{C}_2\text{O}_4)_2]^-$ by increasing acid concentration, and then reaches to equilibrium state forming $[\text{Fe}^{3+}\text{HC}_2\text{O}_4]^{2+}$. In the present system, equilibrium was attained by increasing oxalic acid concentration from 0.01 M to 0.1 M, which refers to a decrease in pH of the leaching system from pH 2 down to pH -0.5. In this stage, cited chemical change was thought to occur. Above 0.1 M oxalic acid concentration dissolution rate of iron stabilized whit the dominating complex ion phase of $[\text{Fe}^{3+}\text{HC}_2\text{O}_4]^{2+}$ (Cornell et al, 1987; Litter et al, 1988; Panias et al, 1996; Torres et al, 1989).

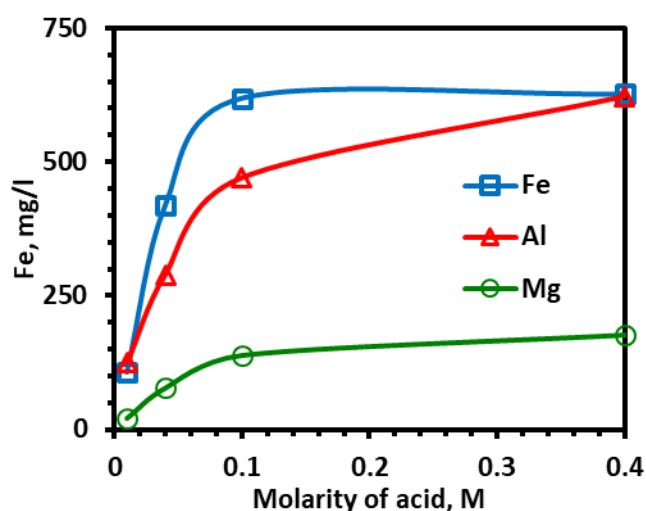


Figure 1. Variation in rejected metal concentration in leach liquor at different oxalic acid dosages

Rejection rate of Al and Mg also increased up to 0.1 M acid concentration. But, further increase was also observed in Al dissolution. Christodoulou et al (2001) proposed that dominating complex ion phase was $[Al_3(OH)_4]^{5+}$. By increasing the acidity, the complex Al ion - $[Al_3(OH)_4]^{5+}$ was thought to convert into $[Al_{13}O_4(OH)_{24}]^{7+}$ as going from pH 2 for lowest tested oxalic acid concentration (0.01 M) to pH -1 for the highest one (0.4 M). Mg ion concentration in the leach liquor was reasonably low as compared to that of Fe and Al. Mg ion was thought to come from mica minerals while Al was mainly assigned to albite ($NaAlSi_3O_8$). Such a lower rate of Mg rejection was explained with the lower mica grade of quartz ore. Mg was also thought to be leached as complex ions by complexing agents- oxalic acid (Zhong et al., 2014).

The increase in the rejection rate of the metal resulted in an improvement in the degree of brightness of quartz ore. Figures 2-4 show the relationship between the color index “L”, “a” and “b” values and the rejection rates of the target metals. The “L” value increased linearly with increasing the iron rejection rate. This linear relationship was also observed for “b” value, which is the measure of yellowness. Decrease in “b” value with an increase in “L” value was referred to rejection of ferric impurities. Ferric species imparts an orange color to quartz ore (Ubalini et al, 1996). The “L” and “b” curves drawn for Mg and Al displayed a parabolic relationship. These responses indicated that Fe rejection rate was directly proportional with whiteness and yellowness although effects of Al and Mg on them were limited.

Curves showing the relationship between “a” value and rejection rates of target metals were obtained in a dissimilar manner. Dissolution of metals at first increased proportionally with the “a” value. Above a limit, increased rate of metal rejection did not reflect on the “a” value. Impurities were thought to be present either as coatings or as free particles. Some of coloring impurities might not be leached due to mineralogical composition in the reducing environment created by oxalic acid (Tuncuk & Akçil, 2014). Some minerals need oxidizing environment to dissolve while some others can be leached in reducing environment (Cepriá et al., 2003; Chiarizia & Hortwiz, 1991; Lee et al., 2007; Veglió et al., 1998). Moreover, coloring impurities as coatings having nanometer size thickness were thought to be removed by oxalic acid leaching up to an acceptable level whereas free particles could not be dissolved completely. Counting tests proved the presence of dark colored particles in the leached samples (Figure 5): number of yellow and black colored particles were determined from a distinct volume of sample which was spread over a unit flat surface area. Number of yellow and black colored particles was so high in the leached quartz sample with 0.01 M oxalic acid that they could not be counted. Then, the counted number for them was taken as 100 for line drawings given in Figure 5. The curves were obtained in

descending order as the concentration of acid increased. But colored particles could not be completely removed even at the highest dosage possible due to presence of free dark colored particles in addition to minerals requiring oxidizing environment to be leached (Cepriá et al., 2003; Chiarizia & Hortwiz, 1991; Lee et al., 2006; Veglió et al., 1996).

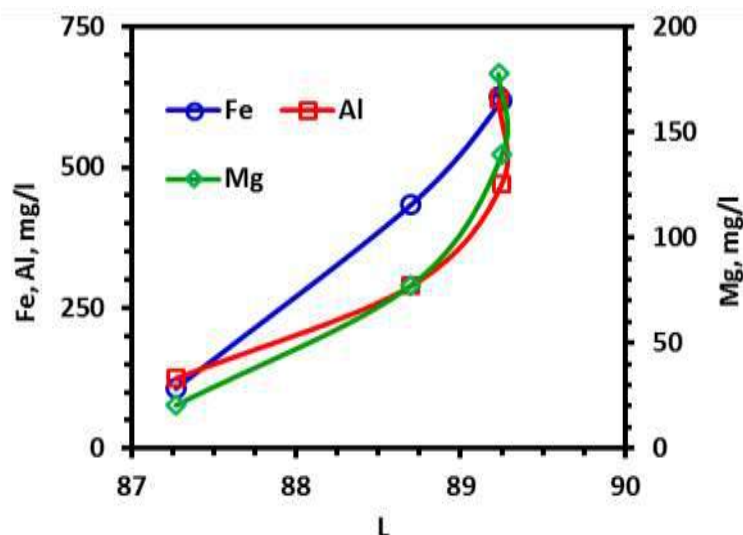


Figure 2. Relationship between rejected metal concentration in leach liquor and color index “L” value response of bleached quartz sample

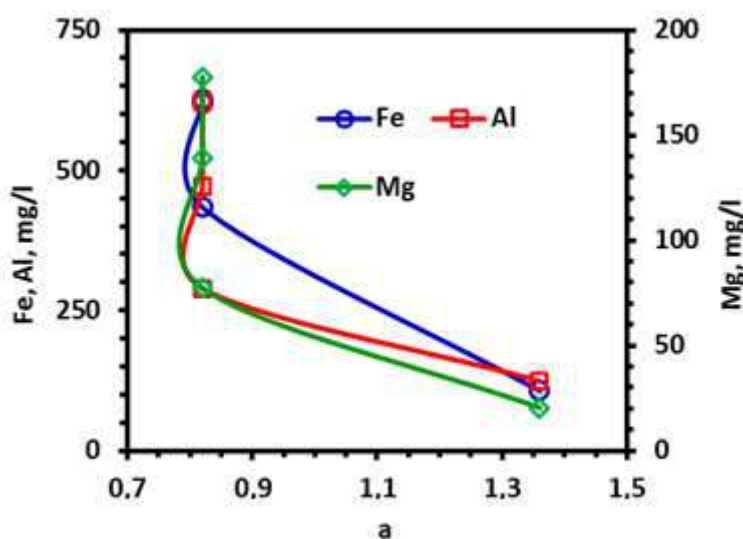


Figure 3. Relationship between rejected metal concentration in leach liquor and color index “a” value response of bleached quartz sample

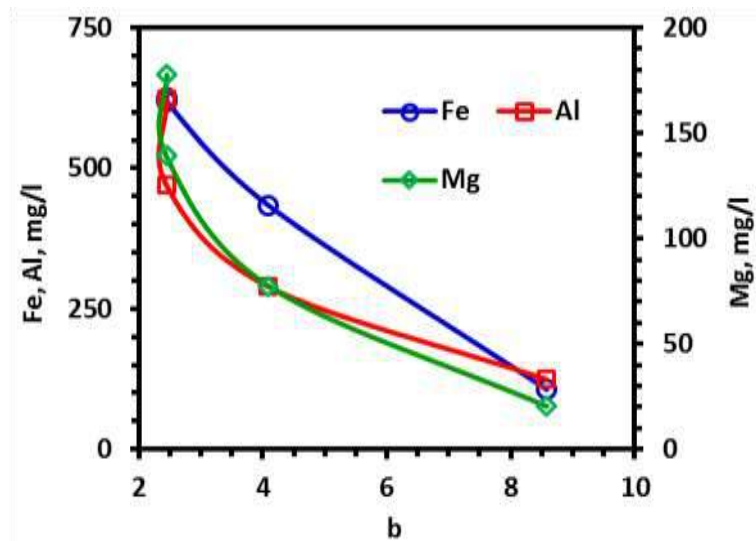


Figure 4. Relationship between rejected metal concentration in leach liquor and color index “b” value response of bleached quartz sample

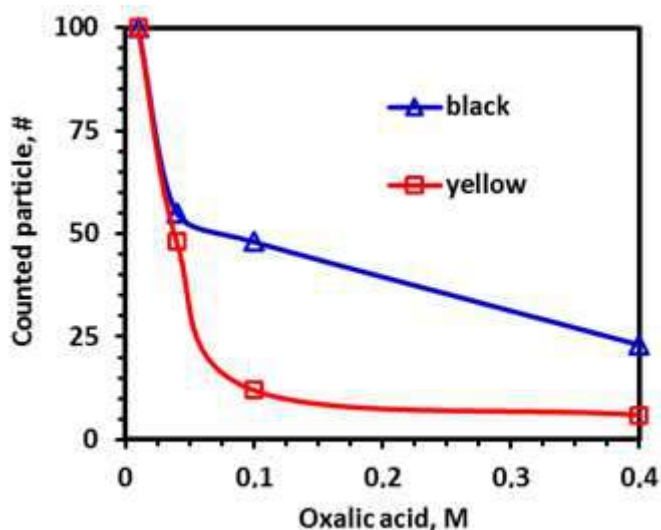


Figure 5. Variation in the number of colored particles in the leached quartz sample with respect to oxalic acid concentration

Metal dissolution rate came to closer to equilibrium dissolution rate at 0.1 M acid concentration (Figure 1), but improvement at the brightness index values above 0.04 M dosage was not so high (Figure 2-4): the “L” value of sample was increased from 80.02 to 88.70 with 0.04 M oxalic acid, and reaches to 89.23 at the highest dosage. The “a” value decreased from 4.28 to 0.82 at 0.04 M dosage, above which it did not change. Those were 17.31, 4.09 and 2.45 for “b” value, respectively. From the comparative evaluation of metal dissolution and brightness index values, investigation on the effect of temperature on bleaching was decided to be performed at 0.04 M oxalic acid concentration. Dissolution of metal ions drew parabolic curve with respect to temperature (Figure 6): metal dissolution increased slightly from 80°C to 90°C, above which change became sharper. Increase in the dissolution rate of Al and Mg above 90°C was more reasonable than that of Fe. On the other hand, improvement rate on the brightness index values “L” and “b” was slightly better for the temperature change from 80°C to 90°C (Figure 7). The “L” value was 88.70, 89.11 and 89.18 for 80°C, 90°C and 95°C while “b” was 4.09, 3.52 and 3.16, respectively. Experimental results revealed that improvement in the brightness was dependent more to

the Fe-rejection. Interesting data was observed on “a” value: bleaching temperature did not cause almost any change (0.82, 0.80 and 0.82 for 80°C, 90°C and 95°C, respectively). Quartz impurities exhibit different leaching behaviors affecting color index “a” value response of material as explained above (Cepriá et al., 2003; Chiarizia & Hortwiz, 1991; Lee et al., 2007; Veglió et al., 1998). Then, some of them was thought not to be leached sufficiently. Additionally, presence of dark colored particles in the leached samples might also contribute onto such results.

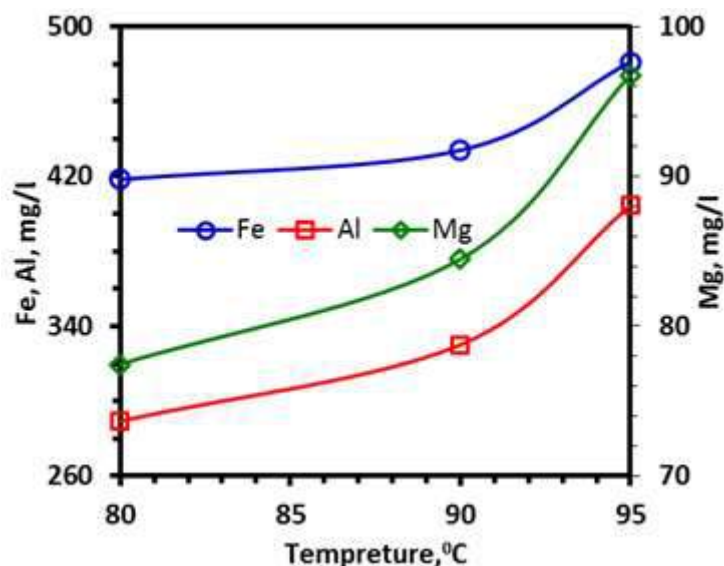


Figure 6. Effect of leaching temperature on the rejected metal concentration in leach liquor

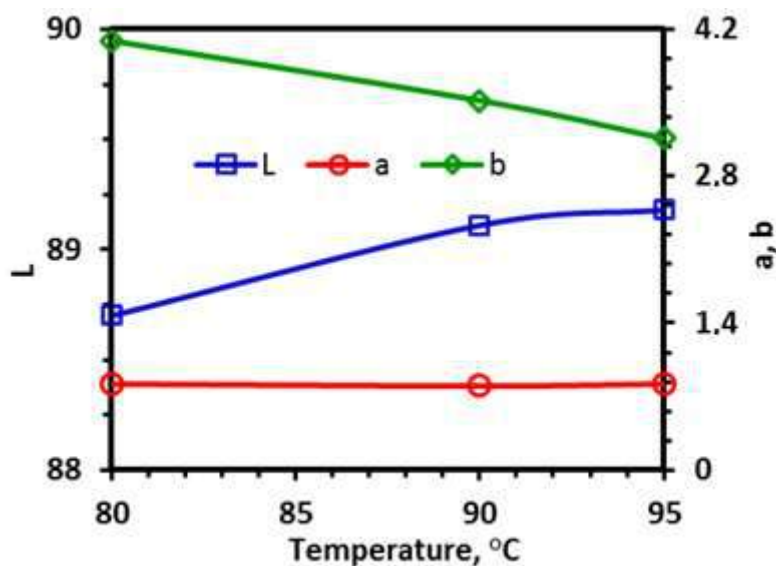


Figure 7. Effect of leaching temperature on the color responses of bleached quartz

CONCLUSIONS

Quartz bleaching by oxalic acid was investigated to clarify the effect of metal (Fe, Al, Mg) rejection rates on the color response. Following conclusions were drawn from experimental works:

- Characterization tests conducted by XRD, SEM and optical microscopy on the quartz ore sample revealed that essential impurities were hematite, magnetite, albite, mica, ilmenite and rutile.
- Rejection rate of metals was observed to be oxalic acid dependent phenomenon: it reached to breaking point at 0.1 M concentration, above which increase in dissolution rate was not reasonable especially for Fe and Mg
- Color analysis demonstrated that Fe rejection rate was directly proportional with whiteness and yellowness although effects of Al and Mg on them were limited.
- Some of the impurities could not be leached in reducing environment created by oxalic acid. They thought to require oxidizing condition to be dissolved.
- Dissolution rates of metals increased reasonably at higher temperatures drawing parabolic curve. However, color response did not exhibit similar trend due possibly to the presence of free dark colored particles.
- Brightest quartz was obtained at 95°C with 0.4 M oxalic acid after 90 min of bleaching. Color responses of bleached sample was measured as 89.18, 0.82 and 3.16 for “L”, “a”, “b”, respectively.

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