ROLE OF CALCIUM CONTENT IN DISSOLUTION KINETICS OF IRANIAN BORATE MINERALS IN SULFURIC ACID

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Abstract   The dissolution kinetics of pandermite and hydroboracite, present in an Iranian borate ore, in sulfuric acid has been comparatively studied. The effect of particle size, temperature, and acid concentration on their dissolution rate was investigated. Dissolution rates of both minerals increased by reducing the particle size and by raising the temperature. Although, an increase in the acid concentration from 0.5 to 1 N accompanied an increase in the dissolution rate, the concentration beyond 1N did not produce any significant change. The dissolution of hydroboracite occurred appreciably faster than pandermite, which was attributed to its lower calcium content. This could be due to the formation of a product layer namely, $CaSO_4.2H_2O$, acting as a diffusion barrier, which in the case of hydroboracite was less effective. The rate data obtained was in agreement with a kinetic model proposed for diffusion- controlled heterogeneous reactions.

Key Words   Borate, Pandermite, Hydroboracite, Dissolution

چکیده   کیتنیک انحلال کانی های پاندرمیت و هیدروبوراسیت موجود در سنگ معدن برات ایران در اسید سولفوریک بطور مقایسه ای مورد مطالعه قرار گرفته است. تاثیر اندازه ذرات، دما و غلظت اسید بر سرعت انحلال بررسی گردید. نتایج نشان داد که سرعت انحلال هر دو کانی با کاهش اندازه ذرات و بالا رفتن دما افزایش می‌یابد. افزایش غلظت اسید از ۰/۵ تا ۱ نرمال منجر به افزایش سرعت انحلال گردید. در صورتیکه در غلظت های بالاتر تغییرات قابل توجهی در روند انحلال کانیها مشاهده نشد. کانی هیدروبوراسیت بسیار سریعتر از پاندرمیت تحت انحلال قرار گرفت که این امر می‌تواند به مقدار کلسیم کمتر موجود در هیدروبوراسیت مربوط باشد. در واقع تشکیل لایه دیفیوزونی$CaSO_4.2H_2O$برسطح ذرات کانی در حین واکنش, مقاومتی در برابر انحلال کانی ایجاد می‌کند که در مورد هیدروبوراسیت تاثیر کمتری را بروز می‌دهد. کیتنیک انحلال هر دو کانی بر اساس مدل کیتنیکی پیشنهاد شده برای واکنشهای هتروژن کنترل شونده توسط عامل دیفوزیون مورد بررسی قرار گرفت و نتایج کیتنیکی بدست آمده را بخصوص در زمانهای اولیه انحلال تایید نمود.

1. INTRODUCTION

More than 150 species of borate minerals are known among which the minerals, borax ($Na_2B_4O_7.10H_2O$), colemanite ($Ca_2B_6O_{11}.5H_2O$), ascharite ($MgBO_2(OH)$), ulexite ($NaCaB_5O_9.8H_2O$), probertite ($NaCaB_5O_9.5H_2O$), hydroboracite ($CaMgB_6O_{11}.6H_2O$) and pandermite ($Ca_4B_{10}O_{19}.7H_2O$) are treated as the major sources of boron in various regions of the world [1].

Extraction of boron from borate ores is generally carried out through as initial dissolution process followed by its subsequent recovery from the leaching solution. Dissolution of some borate minerals with various acids has been investigated and depending upon the kind of the mineral and the acid used, different kinetic processes have been observed. In some of the studies, formation of boric acid film [2-5] or a hard to dissolve product layer like $CaSO_4.2H_2O$ [6] affects the dissolution kinetics whereas, in certain few cases, chemical reactions are found to be the major rate limiting factors [7,8].

As some borate ores may contain various minerals, in order to plan for an appropriate extraction process, it would be necessary to study their comparative dissolution kinetics. In this regard, an Iranian borate ore containing the minerals, pandermite ($Ca_4B_{10}O_{19}.7H_2O$) and hydroboracite ($CaMgB_6O_{11}.6H_2O$) is the subject of such an investigation. Dissolution kinetics of pandermite in sulfuric acid solution has been

already studied [6] and the inhibiting effect of the product layer, $CaSO_4.2H_2O$, on the dissolution process evaluated. Since hydroboracite also contains calcium, an attempt is made to study its dissolution kinetics in comparison to pandermite. The effect of parameters such as particle size, temperature, and the acid concentration on the dissolution rate of these minerals are thus investigated.

2. EXPERIMENTAL

2.1 Materials The borate ore used in this study was from a mine in Gharagol region of Zanjan province. The minerals which were initially sorted out by hand according to their outward appearance in the ore sample were identified by XRD analysis as pandermite and hydroboracite.

The mineral samples were then separately crushed and ground to get various size fractions in the range 250-841 µm. They were then analyzed for elemental determination by ICP-AES method which led to the chemical compositions given in

TABLE 1. Chemical Composition of the Borate Minerals.

Mineral sample	CaO	MgO	B₂O₃
Pandermite	31.41	__	49.36
Hydroboracite	12.42	8.56	51.97

Table1.

The sulfuric acid supplied by Merck and distilled water were used throughout the experiments.

2.2 Method Dissolution experiments were carried out in a one-liter cylindrical glass reactor placed in a thermostatic water bath. A glass stirrer, a thermometer, and a solution sampler could be introduced through the ports in the lid of the reactor. In each experiment, 5g of the sample were added to the reaction vessel containing 500 ml sulfuric acid solution of desired concentration. The stirring speed was adjusted to keep the mineral particles in proper suspension (~600 rpm). Most of the experiments were carried out under fixed process conditions, namely; 420-596 µm mineral
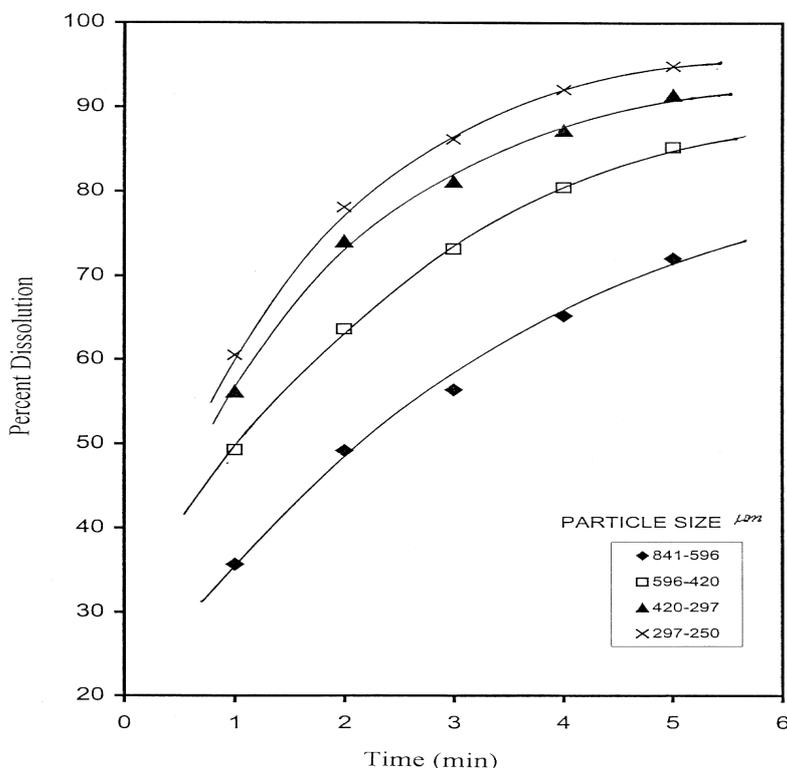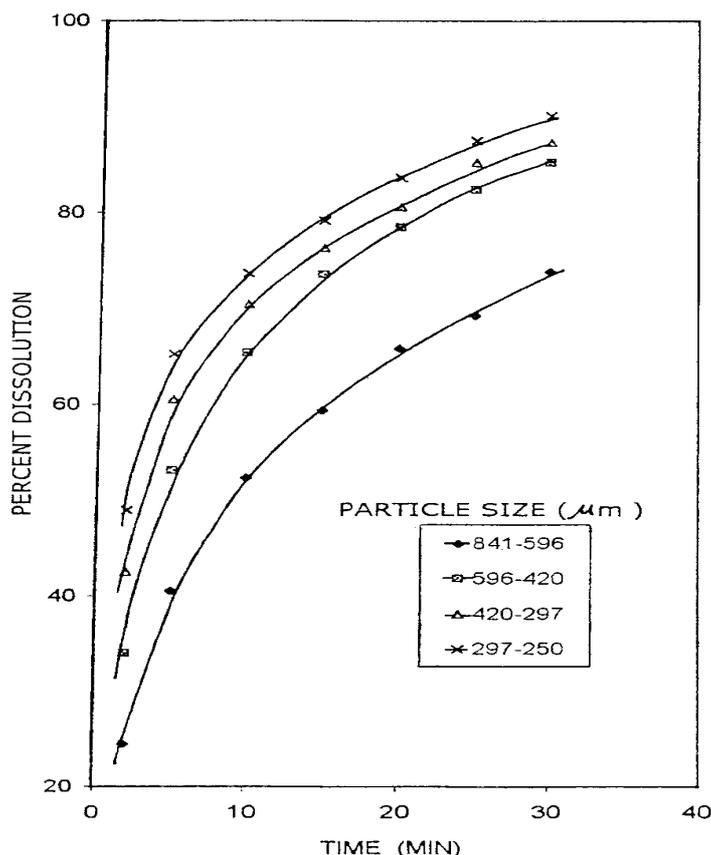

Figure 1. Dissolution of hydroboracite in sulfuric acid solution with various particle sizes.

Figure 2. Dissolution of pandermite in sulfuric acid solution with various particle sizes.

particle sizes, 1 N acid concentration, 1% solid concentration (W/V) and room temperature (~21 ± 1°C). In case of any change in the experimental conditions, it would be mentioned accordingly.

A known volume of the reaction mixture was withdrawn at fixed time intervals and filtered immediately. The filtered sample was diluted and analyzed by ICP-AES to determine B, Ca and Mg content of the leach liquor.

3. RESULTS AND DISCUSSION

3.1 Dissolution of Pandermite ($Ca_4B_{10}O_{19}.7H_2O$)   Dissolution kinetics of pandermite in sulfuric acid, as mentioned earlier, has been studied elsewhere [6]. The effect of

parameters such as particle size, temperature and the acid concentration on the dissolution rate was experimentally evaluated.

The experimental results showed that when the mineral particle size reduced and temperature rose up, the dissolution rate increased, whereas the acid concentration didn't affect the rate significantly. The rate was initially fast, but slowed down after a certain amount of the mineral had been dissolved. It was observed that the dissolution was nearly completed within 30 minutes.

To identify the product species formed during the dissolution process, the unreacted and partially reacted samples were analyzed by XRD and SEM techniques which indicated the presence of the product layer, $CaSO_4.2H_2O$, on surface of the reacting particles. This layer, which was not easily dissolved, acted as a diffusion barrier to limit the dissolution rate. To confirm this, the kinetic model
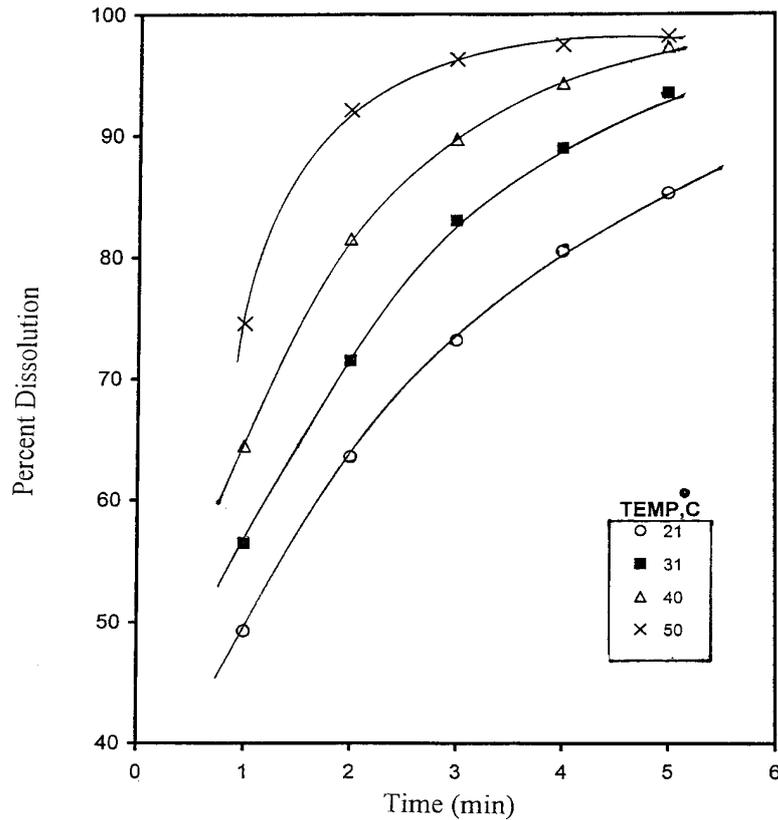
Figure 3. Dissolution of hydroboracite in sulfuric acid solution at different temperatures.

developed by Wadsworth [9], for diffusion-controlled heterogeneous reactions, was used to fit the rate data. The model could describe the kinetics at the initial stage of the dissolution process, however, a deviation from the model was observed due to the thickening of the product layer. This resulted in a reduction of the dissolution rate.

3.2 Dissolution of Hydroboracite (CaMg $B_6O_{11}.6H_2O$) Experiments on the dissolution of hydroboracite was carried out under similar conditions to those of pandermite. The effect of the parameters such as particle size, temperature, and the acid concentration on the dissolution rate was thus investigated.

3.2.1 The Effect of Particle Size Particle size fractions 596-841, 420-596, 297-420 and 250-297 μm were used in this set of experiments while keeping the other parameters constant. The results are presented in Figure 1 where the percent

dissolution of hydroboracite is plotted versus time. It can be seen that the dissolution rate increases as the particle size is reduced. It is also noted that the increase in the rate is less significant for finer particles. It can be further observed that the reaction is approximately completed within 5 minutes, which indicates that the dissolution rate of hydroboracite is quite higher than that of pandermite. In fact the approximate time required for pandermite to dissolve completely, at similar experimental conditions, was about 30 minutes. For comparison, the results on the dissolution of pandermite with different particle sizes are presented in Figure 2 [6].

3.2.2 The Effect of Temperature The experiments here were carried out at various temperatures of 21, 31, 40 and 50°C. The other parameters were kept at their usual values. The results are presented in Figure 3 where it is observed that the dissolution rate increases with
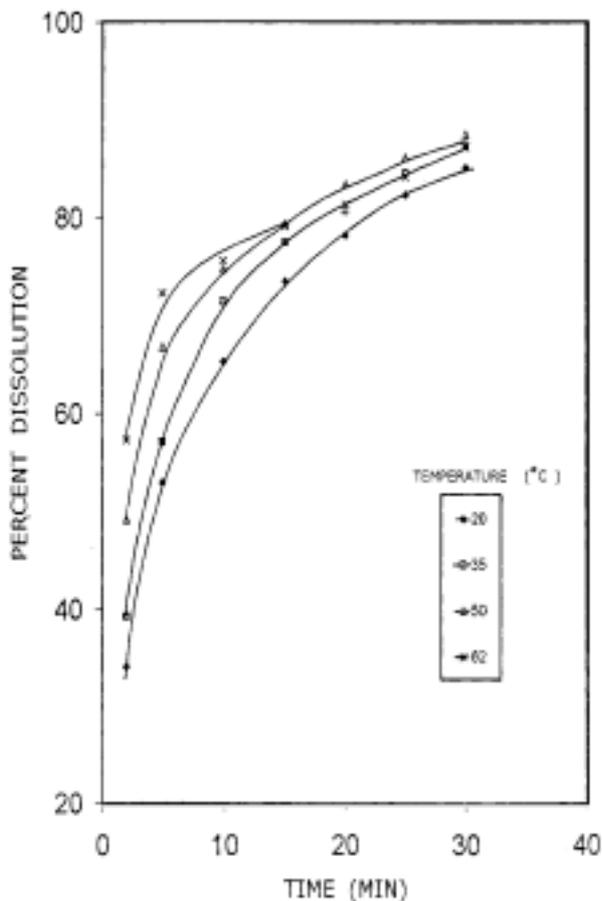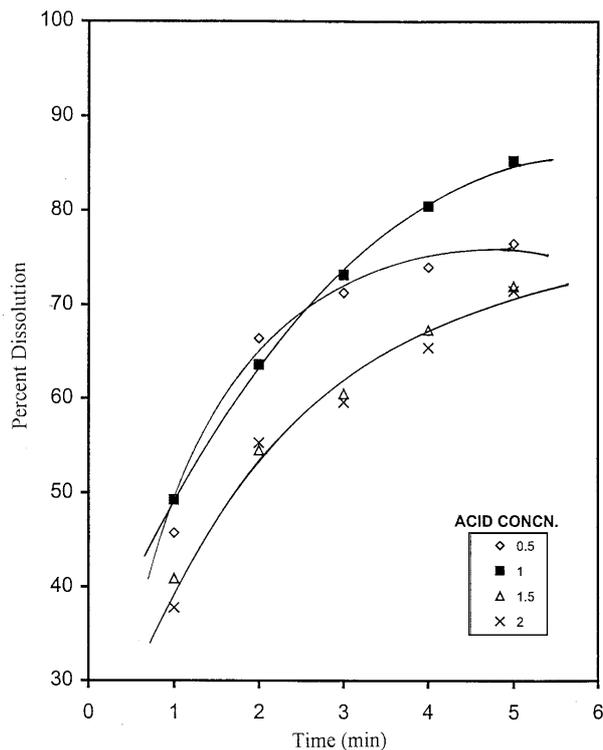
Figure 4. Dissolution of pandermite in sulfuric acid solution at different temperatures.

Figure 5. Dissolution of hydroboracite in various concentrations of sulfuric acid solution.

the temperature. Comparing these results with those obtained for pandermite (Figure 4), it may be noticed that the dissolution of hydroboracite occurs much faster.

3.2.3 The Effect of the Acid Concentration

The concentrations of sulfuric acid used in these experiments varied in the range of 0.5-2N. The results are given in Figure 5. As the figure indicates, an increase in the acid concentration from 0.5 to 1 N results in a higher dissolution rate, however, any further increase in the acid concentration leads to a slight decrease in the rate. It is to be mentioned that a similar behavior was observed in the case of pandermite. This may be due to the higher amounts of sulfate ions produced as the acid concentration increases. In fact, an excess of sulfate ions enhances the formation of

the product layer $CaSO_4.2H_2O$. This compound acts as a diffusion layer that retards the dissolution of such minerals.

3.2.4 Dissolution Kinetics of Hydroboracite

The nature of the rate data and the presence of calcium suggest that diffusion processes can also control the dissolution kinetics of hydroboracite in sulfuric acid, as in the case of pandermite. Therefore, the kinetic model developed by Wadsworth [9] for heterogeneous reactions may be used to fit the rate data. The model is expressed by the following equation:

$$1 - 2/3\ a - (1\text{-}a)^{2/3} = kt$$

where a is the fraction of the mineral reacted, k is a factor related to the rate constant, and t stands for the time. By plotting the terms on the left side of the equation versus time (t), a straight line should result which indicates the validity of the model for the rate data so obtained.
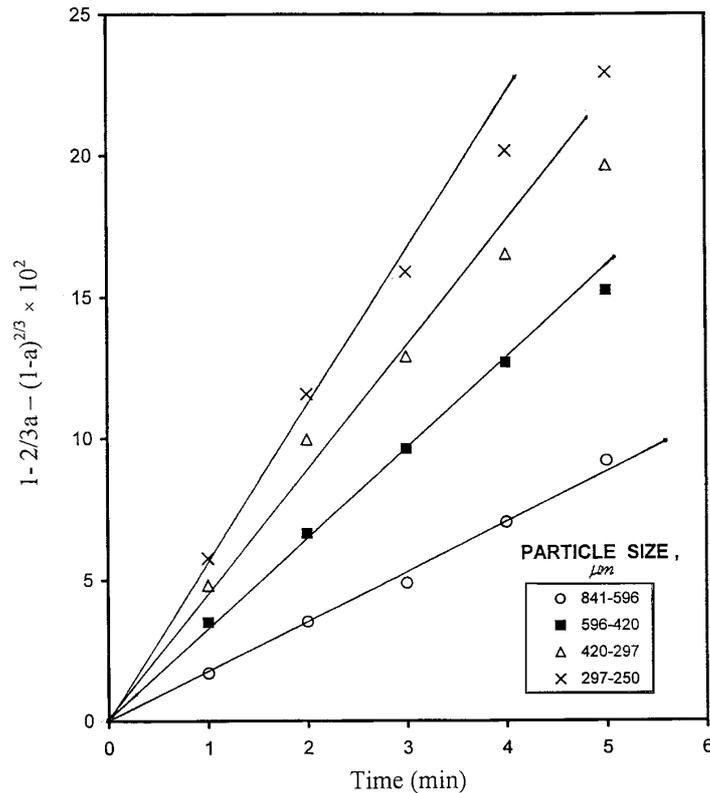
Figure 6. Plots of $1-2/3a-(1-a)^{2/3}$ versus time for the dissolution of hydroboracite with different particle sizes.

These plots for the dissolution of hydroboracite with various particle sizes and at different temperatures are shown in Figures.6 and 7 respectively. It can be seen that a set of straight lines is obtained. It may be noticed that some deviation from linearity occurs for finer particles (Figure 6) and higher temperatures (Figure 7). However, this deviation, which could be attributed to the thickenings of the product layer $(CaSO_4.2H_2O)$, is less significant as compared to the case of pandermite.

4. CONCLUSION

The experimental results obtained through the comparative study on dissolution kinetics of pandermite and hydroboracite, present in the borate ore of Iran, by sulfuric acid, clearly indicate the significance of the product layer formation.

The conclusions, which can be effectively used in processing of such minerals, are:

1.   Reducing the particle size and raising the temperature result in an increase in the dissolution rate whereas, an increase in the acid concentration beyond 1N, dose not affects the rate significantly.

2.   The dissolution of the minerals was initially fast but slowed down at later stages of the process. This was found to be due to the formation of the product layer, $CaSO_4.2H_2O$, as evidenced by XRD and SEM studies discussed in a previous report [6].

3.   The Wadsworth kinetic model, for diffusion controlled heterogeneous reactions, was found to fit the rate data for both minerals satisfactorily. The dissolution kinetics of pandermite and hydroboracite in sulfuric acid are therefore controlled by diffusion through the product layer $CaSO_4.2H_2O$.

4.   Dissolution rate of hydroboracite in sulfuric acid was shown to be much higher than that of pandermite, which can be attributed to the lower amount of calcium
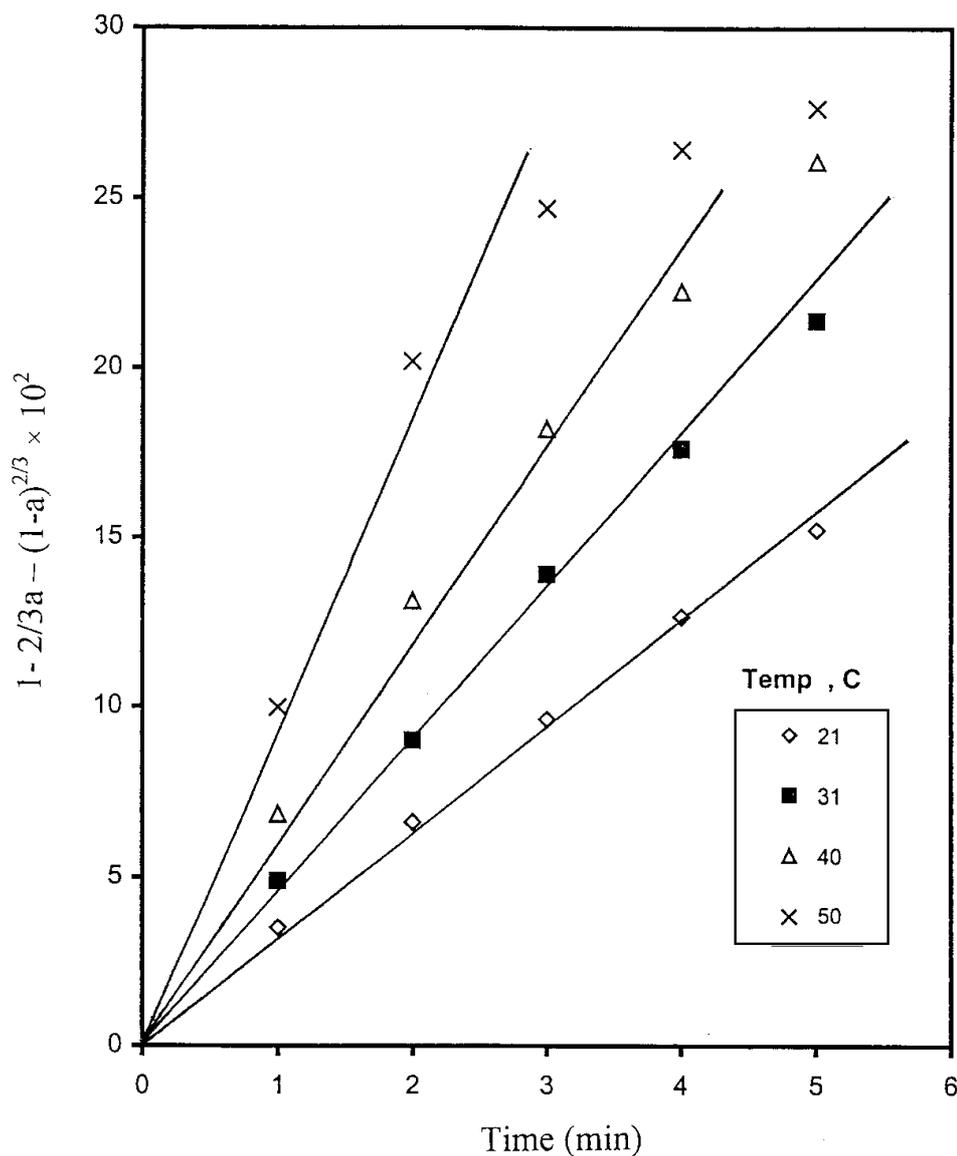
Figure 7. Plots of $1\text{-}2/3a\text{-}(1\text{-}a)^{2/3}$ versus time for the dissolution of hydroboracite at different temperatures.

present in hydroboracite (complete dissolution of hydroboracite takes about 5 minutes as compared to 30 minutes for pandermite). In order to achieve higher efficiency, it therefore seems reasonable to carry out the dissolution process of the above minerals separately.

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