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Non-isothermal microwave leaching kinetics and absorption characteristics of primary titanium-rich materials

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Abstract: The non-isothermal leaching kinetics of primary titanium-rich material by microwave heating was investigated, and the temperature-pressure curves of leaching system and microwave absorption characteristics of mixture solutions before and after leaching were measured. The research of non-isothermal kinetics was evaluated by the leaching rate of Fe and the total apparent velocity equation of the non-isothermal kinetics of leaching for primary titanium-rich material by microwave heating was obtained. It is shown from the temperature-pressure curves that the high temperature and high pressure of closed leaching system are favorable to the enhancement of the leaching rate of Fe. Microwave absorption characteristics of mixture solutions before and after leaching show that there are abrupt changes of microwave absorption characteristics for 15% HCl solution and the mixture solution after leaching by 20% HCl.

Key words: primary titanium-rich material; non-isothermal kinetics; microwave absorption characteristic

1 Introduction

The high quality titanium-rich material is a kind of important raw material for large scale production of high grade rutile-type titanium oxide powder and sponge titanium using chlorination method. Recently, electro smelting, reduction-rusting process and acid leaching have been performed to prepare the high quality titanium-rich material[1−2]. The former two methods were only applied to the special material, which has the low grade of CaO and MgO. In contrast, the acid leaching can deal with all kinds of ilmenite and eliminate the impurity effective. Unfortunately, the conventional acid leaching is characterized by time and energy consumption in order to obtain high grade titanium-rich materials.

To solve the problem, a novel process has shown its advantages, in which the primary rich titanium material can be obtained by using carbothermic reduction-dressing separation of ilmenite, and then the impurities, such as calcium, magnesium, and iron are eliminated by using hydrochloric acid as leaching agent. Comparing with the smelting method of electric arc furnace used at the Panzhihua Steel and Iron Company, this new process has some advantages with lower energy consumption and stronger ability to eliminate impurities like calcium, magnesium and unifying of dressing and smelting, having the feasibility of industrial application prospect[3−4]. Above all, the microwave leaching makes use of the advantage of characteristics such as interior heating, dielectric heating, promoting to make the mineral solid particles burst and exposing the fresh surface of particles[5−8], meanwhile, it is able to promote the high speed vibration of polar liquid molecule, resulting in the increases of mutual collision of materials and enhancement of the liquid-solid reaction rate[9−11].

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In the present study, non-isothermal leaching kinetics of primary titanium-rich materials by microwave heating is studied. The influence of hydrochloric acid concentration, granularity of the primary rich titanium material and the leaching time on the leaching rate of Fe is investigated. The system temperature, the pressure curve and microwave absorption characteristics of mixtures before and after leaching are analyzed, providing some theoretical basis for the new process.

2 Experimental

2.1 Materials

The primary titanium-rich material was obtained using carbothermic reduction by microwave and then dressing separation, its main chemical compositions are 72.01% TiO_2, 9.99% TFe, 4.2% SiO_2, 1.25% Al_2O_3, 9.4% CaO and MgO.

It is shown that the primary titanium-rich material is mainly composed of rutile, and there is little anatase, impurities like calcium and magnesium being concentrated and smelted, although majority of iron is separated, there is still little residue.

2.2 Equipments and methods

The power of microwave test installation is 100−1 000 W, with the frequency of 2.45 GHz; the leaching system's pressure, temperature and time are controllable.

The experimental procedure is as follows: Using 8 g primary titanium-rich material, according to the ratio of liquid to solid of 12:1 (mL/g) to add into hydrochloric acid with a certain concentration. The iron content in the leaching-out liquid was determined by using the potassium bichromate titrimetric method and the titanium dioxide content in the leaching slag was analyzed by using analysis methods for “Ilmenite Ore Concentrate”.

2.3 Principle of test on absorption property

The microwave sensor system was based on the microwave cavity perturbation technique and digital signal processing technique. Derived from the theory of electric-magnetic field, the frequency shift and the output voltage of the microwave cavity were given by[12−13]

$$\frac{\Delta\omega}{\omega}=-\omega_0(\varepsilon_r'-1)\int_{V_e}E_0^*\cdot E\mathrm{d}V/(4W) \tag{1}$$

$$\frac{1}{Q}-\frac{1}{Q_0}=2\varepsilon_0\varepsilon_r''\int_{V_e}E_0^*\cdot E\mathrm{d}V/(4W) \tag{2}$$

$$W=\int_V[(E_0^*\cdot D_0+H_0^*\cdot B_0)+(E_o^*\cdot D_1+H_0^*\cdot B_1)]\mathrm{d}V \tag{3}$$

where $\Delta\omega=\omega-\omega_0$, E_0^*, H_0^* are the hetero conjugations of electric field intensity and electromagnetic field intensity in the resonant sensor before perturbation, respectively, D_0 and B_0 are the hetero conjugations of electric displacement and magnetic induction before perturbation, respectively; V_c and V_e are the volumes of the cavity and the sample, respectively; dV is the elemental volume; Q_0 and ω_0 are the quality factor and resonance frequency of cavity in the unperturbed condition, respectively; Q and ω are the corresponding parameters of the cavity loaded with the sample; ε_r' and ε_r'' are the real and the imaginary part of the complex permittivity of the sample, respectively; W is the storage energy.

From Eq.(1) to Eq.(3), the data of microwave absorbing properties could be acquired by measuring the output voltage and the frequency shift of the microwave sensor. The computer controls the fast scanning microwave generator through multipurpose card. The microwave signals were transmitted into the microwave sensor. The output signals of the microwave sensor were picked up by the linear detector. Then it was fed into the low pass filter. After that, the output signal of the low pass filter was amplified and converted by the A/D converter. The data processing of the microwave sensor system was finished on the computer.

3 Results and discussion

3.1 Determination of non-isothermal kinetics equation and calculation of activation energy

According to Ref.[14], the non-isothermal kinetics equation in microwave field is as

$$\ln\left[\frac{1-(1-\alpha)^{1/3}}{T^2}\right]=\ln\left[\frac{Mc^nAR}{r_0B\rho E}\left(1-\frac{2RT}{E}\right)\right]-\frac{E}{RT} \tag{4}$$

where r is the nucleus radius, r_0 is the primary nucleus radius, c is the concentration, n is the order of reaction, E is the activation energy, A is the frequency factor, M is a constant, T is the leaching system temperature, B is the velocity constant of temperature, ρ is the density of the particles, α is the leaching rate.

According to Eq.(4), the experiments on the relationship between leaching system's temperature and the time in the microwave field, relationship between the leaching rate of Fe in primary titanium-rich material and the time, and relationship between the leaching rate of Fe in titanium-rich material and the temperature were carried out, respectively.

The results show that the temperature of the leaching system increased gradually with increasing microwave heating time. The temperature rising rate equation of leaching system in microwave field is

$$y=3.961\,9x+301.67,\ R^2=0.989\,5 \tag{5}$$

The leaching rate of Fe in primary titanium-rich materials also gradually increased with increasing heating time and temperature, furthermore, during the process, the solution did not reach the constant temperature, and the leaching process was non-isothermal.

The leaching system temperature (T), leaching rate α of Fe and calculated values of the $\ln\{[1-(1-\alpha)^{1/3}]/T^2\}$ were listed in Table 1. Fig.1 shows the relationship between $1/T$ and $\ln\{[1-(1-\alpha)^{1/3}]/T^2\}$.

Table 1 Data derived from non-isothermal leaching kinetics equation

Time/min	T/K	α/%	$\ln\{[1-(1-\alpha)^{1/3}]/T^2\}$
5	287	1.5	−16.86
10	307	5.6	−15.64
15	327	14.8	−14.74
20	347	31.5	−14.02
25	367	55.6	−13.43
30	387	78.0	−13.02
35	407	95.0	−12.60

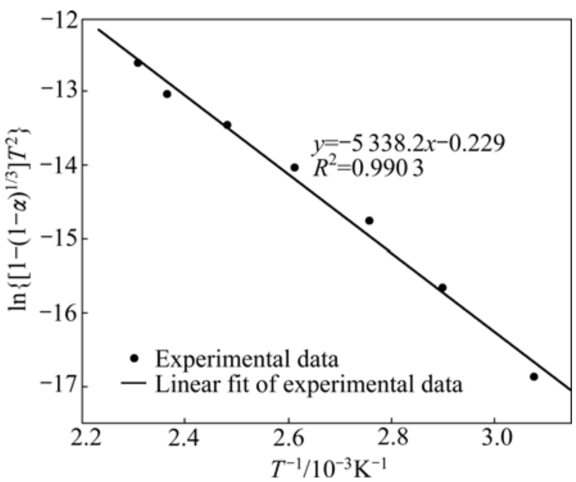

Fig.1 Relationship between $1/T$ and $\ln\{[1-(1-\alpha)^{1/3}]/T^2\}$

According to Arrheniues equation:

$$\ln k_c = -\frac{E_a}{R}\times\frac{1}{T}+\ln A \tag{6}$$

where k_c is the apparent velocity constant.

The apparent activation energy (E_a) within the experiment range for the leaching of primary titanium-rich materials by microwave heating is 44.38 kJ/mol through the fitted curve of Fig.1 and the correlation coefficient is 0.990 3. It is shown by the E_a value that the leaching process of primary titanium-rich material using hydrochloric acid by microwave heating is under control by chemical reaction, indicating that the microwave may promote the mineral solid particle to burst effectively, make the particle expose fresh surface and strengthen the leaching process. This controlling process is different from the results of leaching kinetics of ilmenite in sulfuric acid which is controlled by ore grain's surface reaction and mass transfer resistance of the surface product[15].

3.2 Influence of hydrochloric acid concentration

Fig.2 shows the relationship between leaching rate of Fe^{2+} and leaching time with various concentrations of hydrochloric acid.

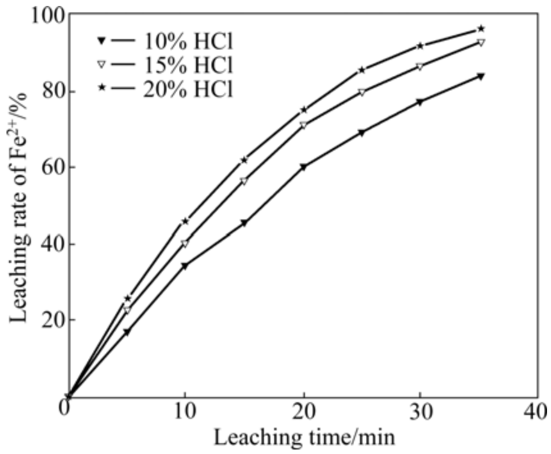

Fig.2 Relationship between leaching rate of Fe^{2+} and leaching time

Using data from Fig.2, the plot of relationship between leaching time and $1-(1-\alpha)^{1/3}$ was obtained, as shown in Fig.3. Through fitted curves of Fig.3, apparent velocity constants (k_c) with different volume fractions of HCl are 0.013 1, 0.016 5 and 0.018 7, respectively, linear correlation coefficients are 0.999 2, 0.999 0 and 0.999 7, respectively. Fig.4 shows the relationship between $\ln[\varphi(\mathrm{HCl})]$ and k_c. The reaction order of leaching primary titanium-rich materials using HCl is 0.505 6 from slope.

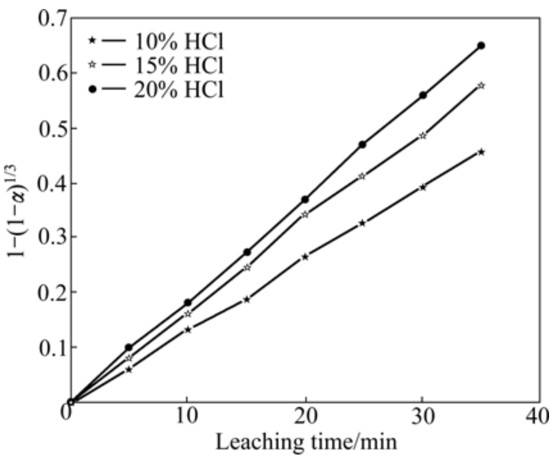

Fig.3 Relationship between leaching time and $1-(1-\alpha)^{1/3}$

HAN et al[16] reported the leaching behavior of ilmenite with sulfuric acid in details and the reaction order was 0.55, the dissolved process was under control by ore grain's surface chemical reaction, which was similar to the result of present study.

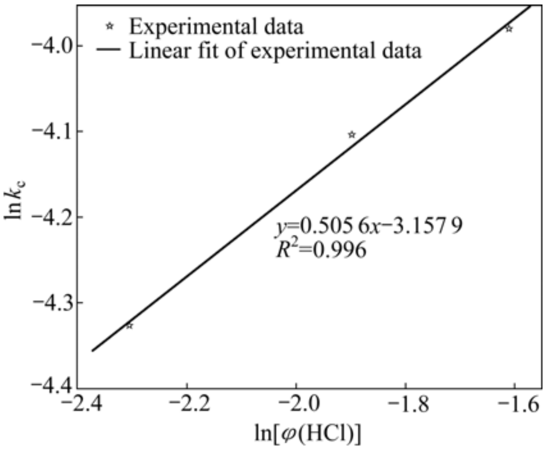

Fig.4 Relationship between ln k_c and ln[φ(HCl)]

3.3 Influence of granularity

Fig.5 shows the relationship between leaching rate of Fe^{2+} and leaching time for titanium-rich material with different grain sizes. Fig.6 shows relationship between $1-(1-\alpha)^{1/3}$ and leaching time of titanium-rich material with different grain sizes using data from Fig.5.

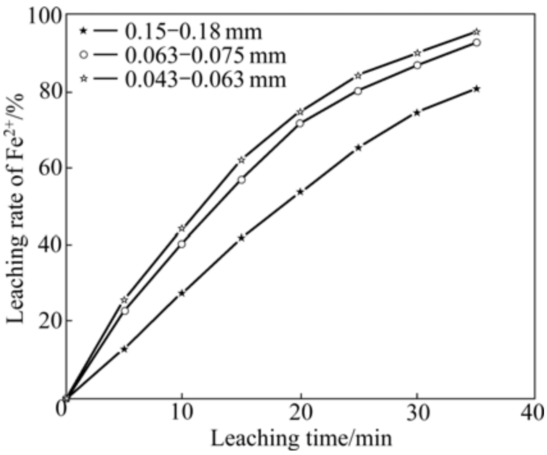

Fig.5 Relationship between leaching rate of Fe^{2+} and time with different grain sizes

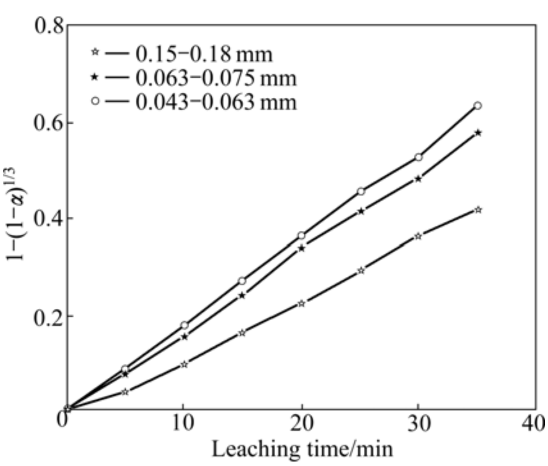

Fig.6 Relationship between $1-(1-\alpha)^{1/3}$ and leaching time with different grain sizes

Apparent velocity constant (k_p) with different particles sizes are 0.012 3, 0.016 5 and 0.018 2, respectively. Fig.7 shows the relationship between $1/r_0$ and k_p. The straight slope and linear correlation coefficient are 5×10^{-4} and 0.998 1, respectively, which indicates the process of leaching with hydrochloric acid by microwave heating is chemical reaction control.

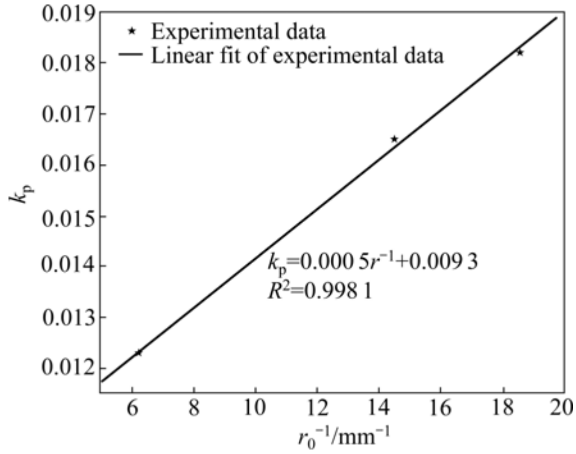

Fig.7 Relationship between k_p and $1/r_0$

3.4 Kinetics equation of leaching primary titanium-rich material using hydrochloric acid

k_c is the apparent reaction constant, relating with reaction system, particle size, the functions of concentration, and can be given by

$$k_c = k_0 c_1^a \cdot c_2^b \cdot c_3^d \ldots r_0^m \cdot \exp\left(-\frac{E}{RT}\right) \quad (7)$$

where k_0 is the velocity constant.

According to the influence of the hydrochloric acid concentration, granularity of the primary titanium-rich material and leaching system's temperature on the leaching rate of Fe^{2+}, and apparent reaction constant k_c obtained at different experimental conditions, the apparent reaction constant k_0 was obtained as 3.51×10^3. Thus, the apparent velocity equation of leaching primary titanium-rich materials using HCl by microwave heating could be approximated by

$$\phi = 3.51\times10^3 r^{-1} \cdot [\text{HCl}]^{0.505\,6} \cdot \exp\left(-\frac{4\,4381.8}{RT}\right) \quad (8)$$

where ϕ is the apparent velocity.

4 Determinations of temperature and pressure curves as well as microwave absorption characteristics

4.1 Leaching system temperature and pressure curves

The relationships between the temperature and pressure of non-isothermal of pure acid solution and leaching system are shown in Figs.8−10.

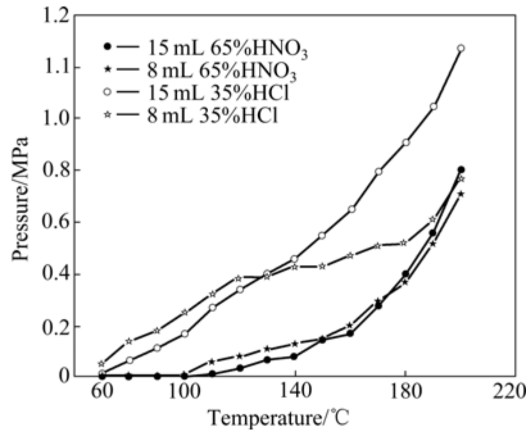

Fig.8 Temperature—pressure curves of acids with different volume fractions

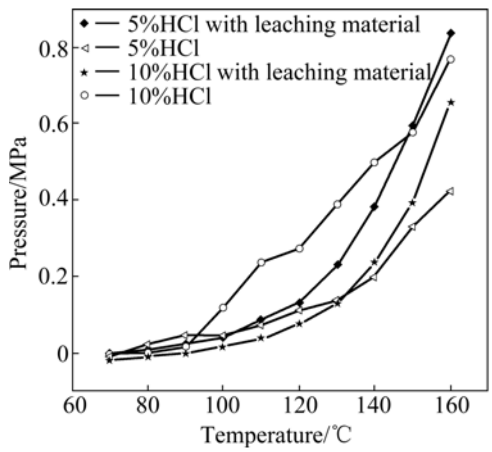

Fig.9 Temperature—pressure curves with or without leaching raw material

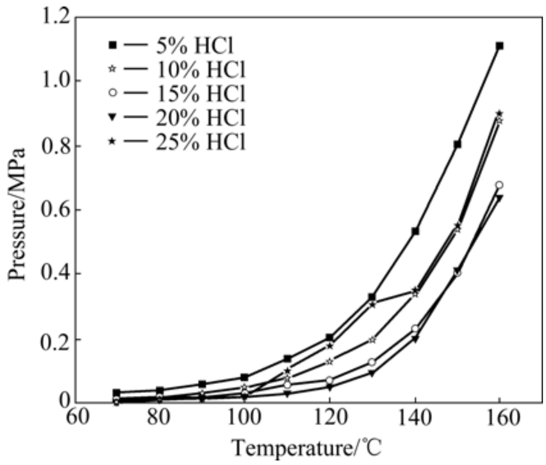

Fig.10 Temperature—pressure curves with leaching raw material

It can be seen from Fig.8 that the system pressures of two leaching agents increases with increasing temperature. The lower the concentration is, the higher the pressure is under the lower temperature. On the contrary, under the higher temperature, the pressure of hydrochloric acid system is higher than that in nitric acid system at same volume fraction and temperature. So, hydrochloric acid is chosen to be leaching agent. Fig.9 shows that the system pressure of 5% HCl is higher than that without leching material at same temperature, inversely, in 10% HCl system, the pressure increases more obviously with increasing temperature in the system with leaching material. Fig.10 shows that the pressure decreases with increasing volume fraction of hydrochloric acid in the system with leaching material from 5% to 20% HCl, which agrees with the experiment results in Section 3.2.

4.2 Absorption characteristics of mixtures before and after leaching

The experiment results of different volume fractions of HCl before and after leaching are shown in Figs.11 and 12. By analyzing the changing rule of the spectrum,

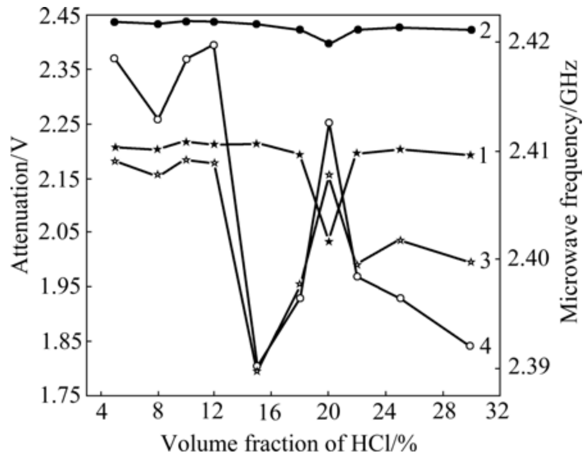

Fig.11 Relationships among attenuation, frequency and volume fraction of HCl after and before leaching: 1—Attenuation before leaching; 2—Microwave frequency before leaching; 3—Attenuation after leaching; 4—Microwave frequency after leaching

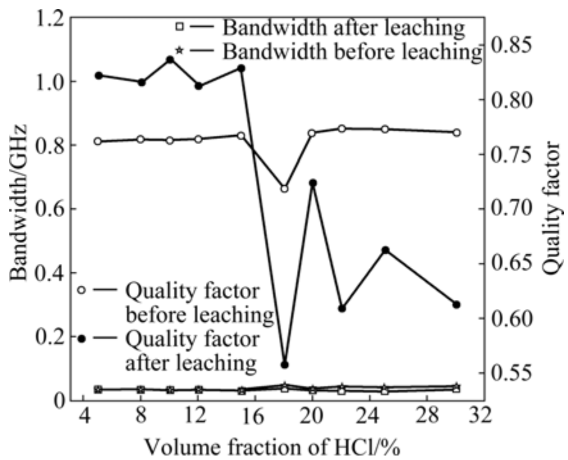

Fig.12 Relationships among bandwidth, quality factor and volume fraction of HCl after and before leaching

the degree of mixture's absorption characteristics in microwave field could be obtained.

Based on the microwave technology, the ε_r'' (complex permittivity) of the mixture is inversely proportional to attenuation change of microwave sensor, ($\varepsilon_r'-1$) of the mixture is directly proportional to frequency shift of microwave sensor, here ε_r' is. Meanwhile, microwave absorbing characteristics is directly proportional to the imaginary part of the complex permittivity. By analyzing the attenuation voltage, frequency, bandwidth and quality factor in Figs.11 and 12, it has shown that there are abrupt changes of microwave absorbing characteristics for 15% HCl leaching solution and mixture after leaching using 20% HCl.

5 Conclusions

1) Non-thermal leaching kinetics of primary titanium-rich material by microwave heating has investigated. The kinetics equation for the leaching primary titanium-rich material by microwave heating is obtained as

$$\phi = 3.51\times 10^{3} r^{-1}\cdot [\mathrm{HCl}]^{0.5056}\cdot \exp\left(-\frac{44381.8}{RT}\right)$$

The apparent velocity constant k_p and $1/r_0$ are in relation to linearity which proved the leaching process for the primary titanium-rich material by microwave heating is under control by surface chemical reaction.

2) The apparent activation energy within the experiment range for the leaching of primary titanium-rich materials by microwave heating is E_a=44.38 kJ/mol. This indicates that the microwave may promote the mineral solid particle to burst effectively, make the particle expose fresh surface and strengthen the leaching process.

3) The determination results of leaching system's temperature and pressure curves indicate that the leaching rate of Fe^{2+} increases with increasing the temperature and pressure. By analyzing the attenuation voltage, frequency, bandwidth and quality factor, it is shown that there are abrupt changes of microwave absorbing characteristics for 15% HCl leaching solution and mixture after leaching using 20% HCl.

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