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Precipitation of Cerium Sulfate Converted from Cerium Oxide in Sulfuric Acid Solutions and the Conversion Kinetics

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The conversion of cerium (IV) oxide into cerium (IV) sulfate in sulfuric acid solutions was studied in a batch-type glass reactor under atmospheric pressure. The effects of agitation speed, acid concentration, reaction temperature, initial amount of cerium (IV) oxide per sulfuric acid solutions (C/S), and particle size on the conversion process were investigated. All experiments were carried out in the range of 8–14 mol/dm^3 for sulfuric acid concentration, 105–135°C for reaction temperature, 0.04–0.28 mol/dm^3 for C/S, and 2.5–112.5 µm for average particle size. The conversion process involves the dissolution of cerium (IV) oxide and the precipitation of cerium (IV) sulfate. Cerium (IV) oxide reacted with sulfuric acid very slowly and then dissolved cerium (IV) in a saturated condition directly formed cerium (IV) sulfate indicating that the conversion rate was controlled by the dissolution rate of cerium (IV) oxide. Increases in sulfuric acid concentration and reaction temperature increased the dissolution rate, whereas increase in particle size decreased it. However, the C/S had no effect on the dissolution rate. In terms of the yield of precipitated cerium (IV) sulfate after reaction equilibrium, increases in sulfuric acid concentration and C/S increased the yield. However, the particle size and the reaction temperature had no effect on the yield of precipitated cerium (IV) sulfate. The kinetics of cerium (IV) oxide dissolution, under various conditions of sulfuric acid concentration, reaction temperature, C/S, and particle size, was interpreted by a shrinking core model with chemical reaction. The variation of rate constant upon dissolution with temperature obeyed the Arrhenius equation with an activation energy of 123 kJ/mol. [doi:10.2320/matertrans.M-M2012826]

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Keywords: *cerium oxide, cerium sulfate, sulfuric acid, conversion kinetics, shrinking-core model*

1. Introduction

Rare earth metal is widely used as a polishing powder for glass, semiconductors and ceramics, and cerium (IV) oxide has become the main element playing a polishing role in rare earth polishing powder. Since cerium (IV) oxide has its own peculiarities such as polishing ability, mechanical strength and wear resistance due to its crystal structure, the production of new types of rare earth polishing material has begun to approach higher cerium (IV) oxide content in solid solutions of rare earth oxides. Numerous investigations have shown that the main feature of highly productive polishing powder is a significant content of cerium (IV) oxide.[1–4]

Commonly, the residues of rare earth polishing powders after the polishing process are not repeatedly used owing to their drainage with polishing liquid or the accumulation of powder such as Al_2O_3, CaO or SiO_2. The residues are converted thoroughly into waste material and most of it is buried in landfill. However, recently, the production scale of polishing powder has been increasing. As a result, the amount of rare earth polishing powder waste (REPPW) produced by the polishing industry have grown.[5]

Rare earth minerals are non-renewable resources, but the demand for them in various fields has been increasing steadily. As such, vigorous investigation into the recovery of rare earth minerals from various types of waste is required globally. Comprehensive recovery processes of rare earth elements as well as cerium (IV) oxide from REPPW can play an important role in resource protection. Despite this background, there have been few reports on the recovery or recycling of REPPW.[6–8]

Pyrometallurgical and hydrometallurgical processes are employed for treating various types of waste. A major disadvantage of pyrometallurgical methods is their high energy requirements and severe corrosion problems (generation of dust and gas). The hydrometallurgical processes, by comparison, are more environmentally suitable and economical to treat waste on a small scale.[9] The acid leaching process, which is one of the hydrometallurgical processes, has some demerits in separation and recovery. For example, undesired species are dissolved along with the materials of interest in the solution and another method is needed to separate these materials. Nevertheless, the leaching process is easy and inexpensive to implement for the treatment of REPPW.

Cerium (IV) oxide can be dissolved in concentrated acid solutions and at elevated temperatures, although it is the most stable phase among the rare earth oxides so there are many difficulties associated with dissolving it in acidic solutions. When using sulfuric acid solutions, cerium (IV) sulfate can be precipitated in acidic solutions by controlling the acid concentration, reaction temperature and so on, which can be an effective way to recover cerium from REPPW. Besides, recovered cerium (IV) sulfate can be useful for various applications; this material has recently received widespread attention for various applications such as in redox flow batteries,[10] and as an oxidimetric agent,[11,12] and a catalyzer.[13]

The aim of this research, therefore, was to study the conversion kinetics of cerium (IV) oxide into cerium (IV) sulfate in sulfuric acid solutions. The experimental data were calculated to confirm the effect of sulfuric acid concentration, reaction temperature, C/S and particle size on the conversion. In addition, the solubility and the yield percentage of precipitated cerium (IV) sulfate in saturated solutions at various conditions mentioned above were also investigated. Furthermore, the conversion kinetics was analyzed and the fitted equation to the experimental data was determined.

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Table 1 Parameters chosen in experiments.

Parameters	Values
Agitation speed (rpm)	150; 250; 550; 650; 750; 900; 1050
Sulfuric acid concentration (mol/dm^3)	8; 10; 12
Reaction temperature (°C)	105; 115; 125; 135
Initial amount of cerium (IV) oxide per sulfuric acid solutions (mol/dm^3)	0.04; 0.12; 0.2; 0.28
Average particle size (μm)	112.5; 47.5; 10; 2.5

2. Experimental Methods

2.1 Process and materials

The cerium (IV) oxide used in this study was chemical grade of 99.9% metal basis (Sigma Aldrich, Ltd.) and the particle size was 3–6 mm. It was crushed, ground, and sieved to give $(-150+75)$, $(-75+20)$, -20, and $-5\,\mu$m size fractions using ASTM standard sieves. All experiments were carried out using $-5\,\mu$m cerium oxide, except for the study on the effect of particle size on conversion.

2.2 Experimental methods

All experiments were carried out by putting the desired amount of cerium (IV) oxide into 100 mL sulfuric acid solutions with various acid concentrations in a batch-type glass reactor of 300 mL kept at a desired temperature on a hot plate stirrer with a thermostat. The solution was stirred by a magnetic stirrer at the desired agitation speed. The parameters used in the experiments were chosen as follows: sulfuric acid concentration, reaction temperature, C/S and particle size. The values of these parameters are given in Table 1.

To identify the crystalline phases of cerium (IV) oxide residue and precipitated cerium (IV) sulfate vs. reaction time during the conversion of cerium (IV) oxide into cerium (IV) sulfate in sulfuric acid solutions, the samples taken at different reaction times were filtered and measured using an X-ray diffractometer (PANalytical, X'pert PRO) for mineralogical analysis.

For measuring the weight of cerium (IV) oxide residue and precipitated cerium (IV) sulfate vs. reaction time, the samples taken at appropriate reaction times were filtered from the solution on a 0.5 μm pore size membrane using a pressure filtration unit, and were washed 3 times using ethanol to remove the sulfuric acid. After drying at 45°C for 24 h, the weight (a) of the precipitate consisting of cerium (IV) oxide residue and precipitated cerium (IV) sulfate was measured using a balance. The precipitate was then placed into sulfuric acid solution (3–4 mol/dm^3) at 90°C to dissolve the cerium (IV) sulfate. The cerium (IV) oxide residue was recovered by filtering. The weight (b) of cerium (IV) oxide residue was measured using a balance after drying at 45°C for 24 h. The difference between (a) and (b) determined the weight of participated cerium (IV) sulfate.

3. Results and Discussion

3.1 Conversion reaction

Two chemical reactions are considered to be involved in the conversion of cerium (IV) oxide into cerium (IV) sulfate in sulfuric acid solutions as follows.

Cerium (IV) oxide reacts with sulfuric acid at atmospheric pressure according to the following dissolution reaction:

$$CeO_2 + 4H^+ \rightarrow Ce^{4+} + 2H_2O. \quad (1)$$

At high sulfuric acid concentrations, the concentration of mixed cerium (IV) exceeds its solubility at an early stage. Then, cerium (IV) cations dissolved under saturated conditions directly form cerium (IV) sulfate as follows:

$$Ce^{4+} + 2SO_4{}^{2-} \rightarrow Ce(SO_4)_2. \quad (2)$$

Cerium (IV) cations can be reduced to cerium (III) cations as follows:

$$Ce^{4+} + 1/2H_2O \rightarrow Ce^{3+} + H^+ + 1/4O_2. \quad (3)$$

It can be estimated that this reaction proceeds much less than the cerium (IV) sulfate formation according to the following experimental results.

3.2 Effect of agitation speed

Before studying the effect of other factors on the conversion of cerium (IV) oxide into cerium (IV) sulfate in acidic solutions, the effect of the agitation speed was first studied. This experiment was carried out at agitation speeds ranging from 150 to 1050 rpm using 8 mol/dm^3 sulfuric acid solutions at 125°C for 24 h reaction time. The C/S was 0.04 mol/dm^3 and cerium (IV) oxide with 2.5 μm average particle size was used. It was found that the dissolution of cerium (IV) oxide increased with increasing agitation speed and became almost independent of the agitation speed at rpm higher than 750 rpm. Therefore, subsequent experiments were performed at 750 rpm.

3.3 Effect of sulfuric acid concentration

The effect of sulfuric acid concentration, in the range from 8 to 12 mol/dm^3, on conversion at 125°C was examined. The C/S was 0.2 mol/dm^3 and cerium (IV) oxide with 2.5 μm average particle size was used. As seen in Fig. 1, the result shows that the dissolution rate of cerium (IV) oxide increased with increasing sulfuric acid concentration and dissolved cerium (IV) cations in acid solutions directly formed cerium (IV) sulfate. The concentration of cerium (IV) sulfate in acid solutions exceeded its solubility and cerium (IV) sulfate was precipitated directly. The amount of cerium (IV) oxide decreased monotonically with increasing reaction time, while the precipitated cerium (IV) sulfate increased; the two reactions were in synchrony. These findings suggest that the reduction of cerium (IV) to cerium (III) is not significant. The XRD patterns of the precipitate provide evidence for the conversion (Fig. 2). The intensity of the diffraction peaks originating from cerium (IV) oxide decreased with an increase in reaction time, while that from cerium (IV) sulfate increased. These results show the procedure of conversion of cerium (IV) oxide into cerium (IV) sulfate clearly and also support the results shown in Fig. 1.

The possible precipitation of cerium (IV) sulfate in acid solutions depends on the solubility limits in terms of acid concentration. Thus, the solubility of precipitated cerium (IV) sulfate in saturated solutions at various acid concentrations

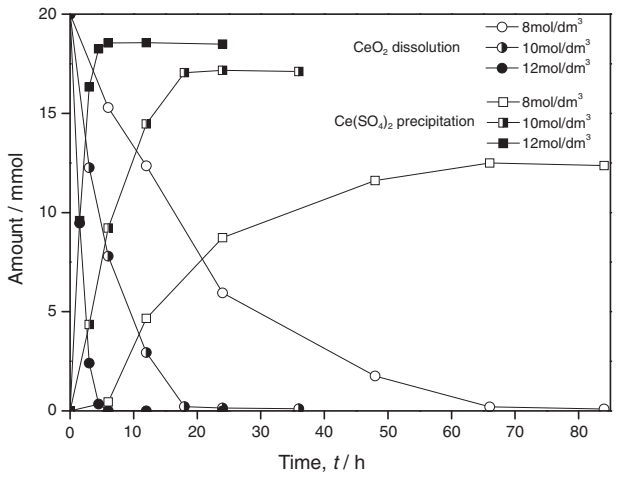

Fig. 1 Effect of sulfuric acid concentration on conversion kinetics of cerium oxide into cerium sulfate in acidic solutions (750 rpm agitation speed, 125°C reaction temperature, 0.2 mol/dm^3 initial amount of cerium (IV) oxide per sulfuric acid solutions, and 2.5 μm average particle size).

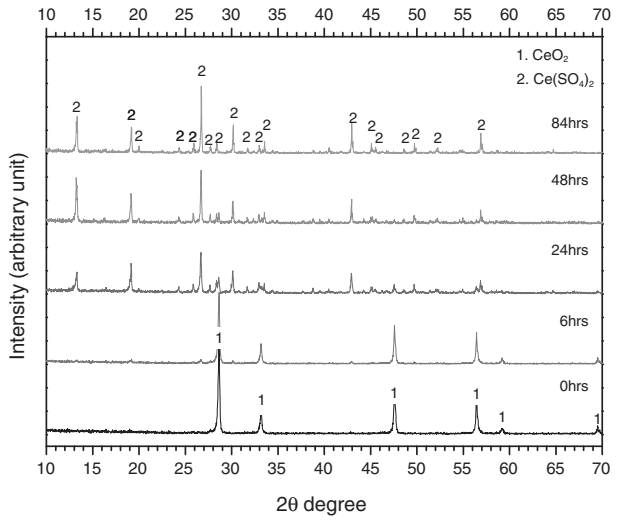

Fig. 2 XRD patterns of the precipitate obtained at different reaction times (750 rpm agitation speed, 8 mol/dm^3 sulfuric acid concentration, 125°C reaction temperature, 0.2 mol/dm^3 initial amount of cerium (IV) oxide per sulfuric acid solutions, and 2.5 μm average particle size).

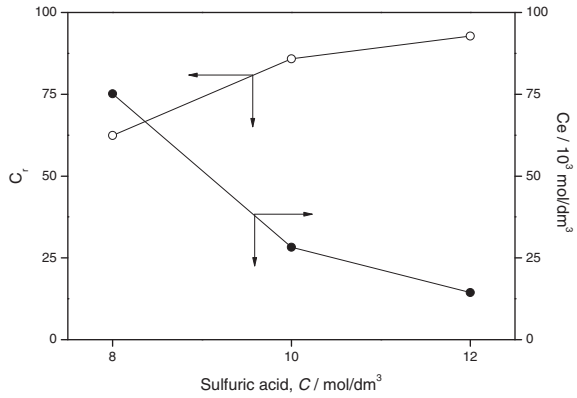

Fig. 3 Effect of sulfuric acid concentration on solubility and yield percentage of precipitated cerium sulfate.

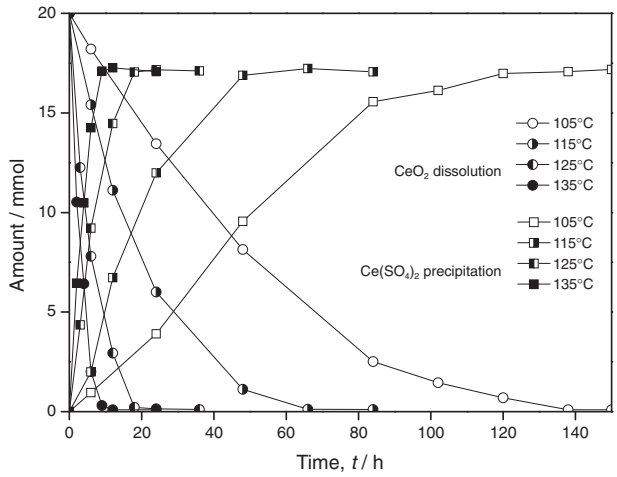

Fig. 4 Effect of reaction temperature on conversion kinetics of cerium oxide into cerium sulfate in acidic solutions (750 rpm agitation speed, 10 mol/dm^3 sulfuric acid concentration, 0.2 mol/dm^3 initial amount of cerium (IV) oxide per sulfuric acid solutions, and 2.5 μm average particle size).

ranging from 8 to 12 mol/dm^3 after the reaction equilibrium was investigated. The solubility of cerium (IV) ions decreased with increasing sulfuric acid concentration, as can be seen in Fig. 3. This can be explained by the well-known "common ion effect": increasing SO_4^{2-} ion concentration will lead to decreased solubility of cerium (IV) sulfate.

In the case of cerium recovery from waste containing cerium (IV) oxide, the precipitation of cerium (IV) sulfate converted from cerium (IV) oxide in sulfuric acid solutions during the leaching process can be one of the most important factors. Therefore, the yield percentage of precipitated cerium (IV) sulfate was investigated using the following equation:

$$C_r = (C_p/C_0) \times 100, \quad (4)$$

where C_r represents the yield percentage of precipitated cerium (IV) sulfate; C_0, the initial amount of cerium (IV) oxide (mol); and C_p, the amount of precipitated cerium (IV) sulfate after equilibrium (mol). In Fig. 3, the yield percentages are also indicated and it is found that increasing sulfuric acid concentration increased the yield percentage of precipitated cerium (IV) sulfate according to decreasing solubility of cerium (IV); the yield rose from 62% at 8 mol/dm^3 to 93% at 12 mol/dm^3.

3.4 Effect of reaction temperature

The cerium (IV) oxide with an average particle size of 2.5 μm was dissolved using 10 mol/dm^3 acid concentration at various temperatures ranging from 105 to 135°C to examine the effect of the reaction temperature on the conversion. Figure 4 shows that the dissolution rate of cerium (IV) oxide and the precipitation rate of cerium (IV) sulfate increased with increasing reaction temperature. The yield percentage of precipitated cerium (IV) sulfate was independent of temperature. Namely, the changing of temperature at high acid concentration has no effect on the solubility and precipitation of cerium (IV) sulfate. In the literature, the dissolution of many salts into aqueous solution is described as an

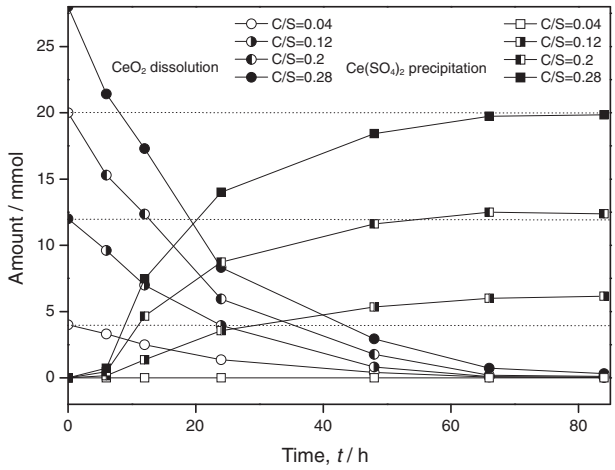

Fig. 5 Effect of initial amount of cerium (IV) oxide per sulfuric acid solutions (C/S) on conversion kinetics of cerium oxide into cerium sulfate in acidic solutions (750 rpm agitation speed, 8 mol/dm^3 sulfuric acid concentration, 125°C reaction temperature, and 2.5 µm average particle size).

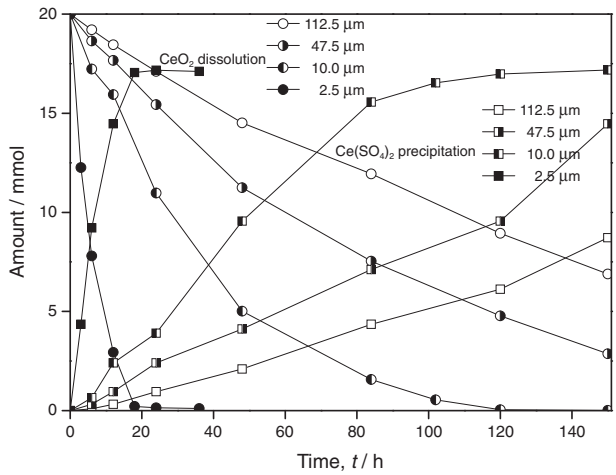

Fig. 6 Effect of particle size on conversion kinetics of cerium oxide into cerium sulfate in acidic solutions (750 rpm agitation speed, 10 mol/dm^3 sulfuric acid concentration, 125°C reaction temperature, and 0.2 mol/dm^3 initial amount of cerium (IV) oxide per sulfuric acid solutions).

endothermic process and increasing temperature increases solubility, whereas the dissolutions of many lanthanide sulfates are reported to be exothermic reactions and rising temperature often results in a sharp decrease in their solubility. However, the effect of temperature on the solubility of cerium (IV) sulfate was most significant at sulfuric acid concentrations less than 2 mol/dm^3 and it was almost negligible at over 4 mol/dm^3 according to Paulenova *et al.* (2002).[10] This result of Paulenova *et al.* is in accordance with the results obtained in this study.

3.5 Effect of initial amount of cerium (IV) oxide per sulfuric acid solutions (C/S)

The effect of C/S on conversion was tested by varying this ratio in the range from 0.04 to 0.28 mol/dm^3. Within these experiments, the initial sulfuric acid concentration and reaction temperature were kept constant at 8 mol/dm^3 and 125°C. Cerium (IV) oxide with an average particle size of 2.5 µm was used. Figure 5 shows that the amount of precipitated cerium (IV) sulfate increased with increasing C/S from 0.12 to 0.28 mol/dm^3, whereas no precipitate existed at 0.04 mol/dm^3. At all C/S employed, the dissolution of cerium oxide was complete after 66 h at an almost equal reaction time, except for the case of 0.28 mol/dm^3. However, the dissolution rate over 0.28 mol/dm^3 could decrease because the sulfuric acid concentration cannot be maintained at 8 mol/dm^3 by stoichiometric decrease of sulfuric acid in solutions. In addition, the increasing C/S increases the suspension density as well as the viscosity of the system and therefore increases the mass transfer resistance in the solid–liquid interface.

Increasing C/S increased the yield percentage of precipitated cerium (IV) sulfate.

3.6 Effect of particle size

The effect of particle size, with average sizes of 112.5, 47.5, 10 and 2.5 µm, on the conversion was examined using 8 mol/dm^3 sulfuric acid solutions at 125°C with C/S of 0.2 mol/dm^3. Figure 6 indicates that the decrease in particle size enhanced the dissolution rate of cerium (IV) oxide with increased contact area. At a smaller particle size, the effect of dissolution rate was more significant than expected. However, the particle size had no effect on the yield percentage of precipitated cerium (IV) sulfate.

3.7 Conversion kinetics

The reaction rate of the conversion of cerium (IV) oxide into cerium (IV) sulfate, in this study, was controlled by the dissolution rate of cerium (IV) oxide because the precipitation rate of cerium (IV) sulfate is much faster than the dissolution rate of cerium (IV) oxide; it took more than 48 h to dissolve 0.02 mol cerium (IV) oxide with an average particle size of 0.5 µm in 100 ml of 8 mol/dm^3 acid solution at 125°C. The dissolution of cerium (IV) oxide in acid solution can be expressed according to the heterogeneous reaction. The fluid-solid heterogeneous reaction process can be expressed by the following model.

The shrinking core model is the most widespread model describing fluid-solid reaction kinetics of dense (non-porous) particles.[14–17] The fluid-solid heterogeneous reaction process may be expressed as certain individual steps such as film diffusion, surface chemical reaction and product layer diffusion control. In this study, experimental data of cerium (IV) oxide dissolution, which was performed under various conditions of sulfuric acid concentration, reaction temperature and particle size, were made to fit the shrinking core model to Ce-dissolution vs. time curves. Assuming that the reaction rate of cerium (IV) oxide dissolution was controlled by the chemical reaction and particle were in a homogeneous spherical solid phase, the data were analyzed using a formula as follows:

$$1 - (1 - X_t)^{1/3} = kt. \tag{5}$$

Here, k is the reaction rate constant (h^{-1}) of cerium (IV) oxide dissolution and X_t is the dissolved fraction vs. time t, which was then calculated as follows:

$$X_t = 1 - W_t/W_0. \tag{6}$$

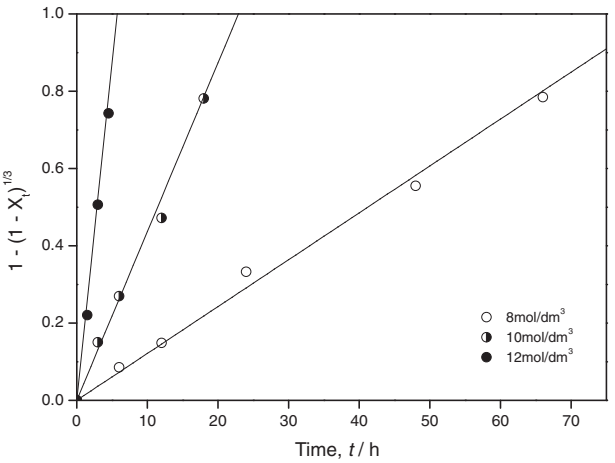

Fig. 7 Plots of $1-(1-X_t)^{1/3}$ versus reaction time for different sulfuric acid concentrations.

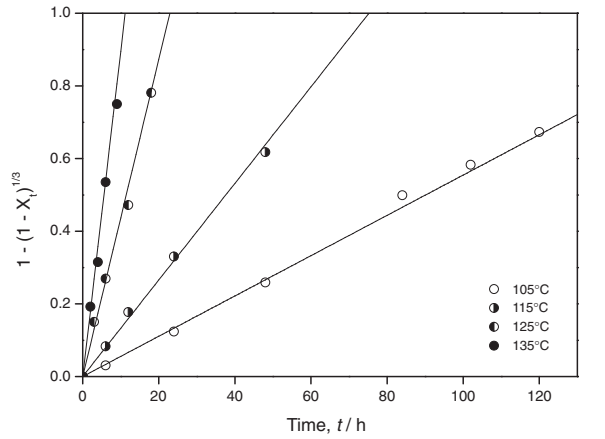

Fig. 8 Plots of $1-(1-X_t)^{1/3}$ versus reaction time for different reaction temperatures.

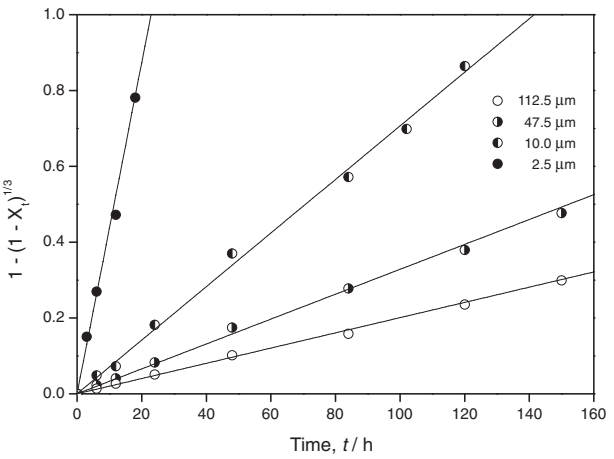

Fig. 9 Plots of $1-(1-X_t)^{1/3}$ versus reaction time for different particle sizes.

Here, W_0 and W_t represent the initial and residual amounts of cerium (IV) oxide vs. time t, respectively. As mentioned above, this model assumes the surface reaction of cerium (IV) oxide with the reactant, H^+, in the solution, and a decrease in the surface area due to the decrease in the initial particle radius with time t. As shown in Figs. 7, 8 and 9,

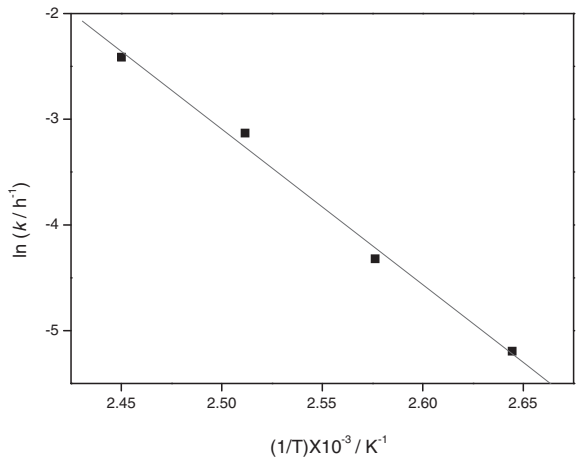

Fig. 10 Effect of reaction temperature on the conversion rate constants.

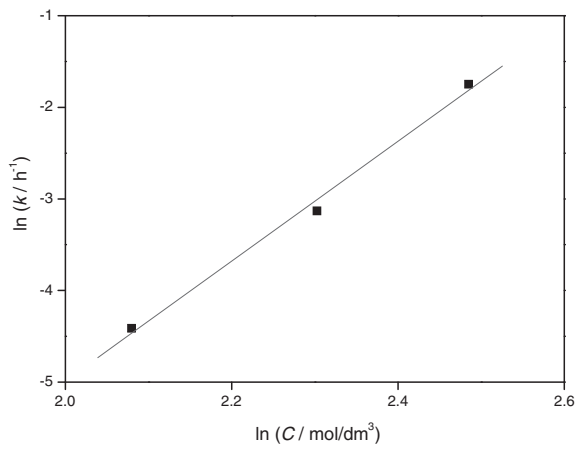

Fig. 11 Effect of sulfuric acid concentration on the conversion rate constants.

$1-(1-X_t)^{1/3}$ plotted against reaction time t is almost a straight line for each experimental condition, with a correlation coefficient more than 0.99, indicating that the dissolution data reasonably followed the shrinking core model. The rate constant k varies with experimental conditions and is the function of reaction temperature, sulfuric acid concentration, and particle size. When cerium (IV) oxide is dissolved into sulfuric acid solutions in all experiments, the dissolution rate constant, considered as the function of reaction temperature, sulfuric acid concentration and particle size, can be expressed by the following equation:

$$k = k_0' e^{-Ea/RT} C^m r^n. \tag{7}$$

Where Ea is the activation energy (kJ/mol); R, the ideal gas constant, 8.314×10^{-3} (kJ/mol K); T, the reaction temperature (K); C, sulfuric acid concentration (mol/dm^3); r, particle size (µm); k_0', pre-exponential factor; and m and n are constants. Linear regressions in Figs. 7, 8 and 9 were used to calculate k values from the slopes. In addition, the $\ln k$ values calculated from these k values were plotted against $1/T$, $\ln C$ and $\ln r$ using equations $k = k_1' e^{-Ea/RT}$, $k = k_2' C^m$ and $k = k_3' r^n$ where k_1', k_2' and k_3' are the pre-exponential factors. The activation energy, m, and n were calculated from the slopes of the lines in Figs. 10, 11 and 12, respectively.

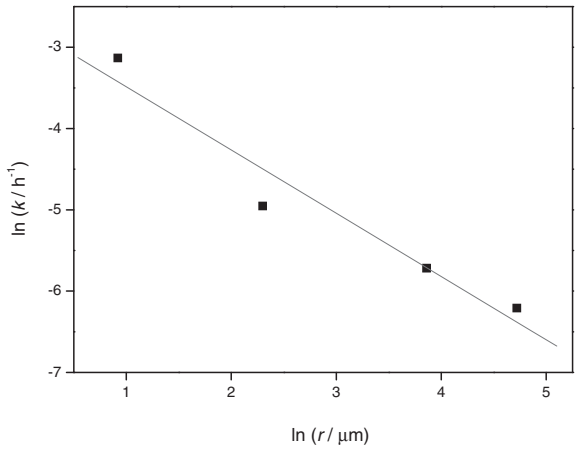

Fig. 12 Effect of particle size on the conversion rate constants.

The slopes in Fig. 7 determined the reaction rate constant related to the sulfuric acid concentration ranging from 8 to 12 mol/dm^3. A plot of $\ln k$ versus $\ln C$ in Fig. 11 shows that the constant m was calculated to be 6.54. This large constant indicates a strong effect of acid concentration on the dissolution rate of cerium oxide. Figure 8 shows the effect of reaction temperature on the dissolution rate of cerium (IV) oxide. The slopes of the experimental data in Fig. 8 were used to determine the reaction rate constants for various temperatures in the dissolution stage. As shown in Fig. 10, the increase in dissolution rate constant with increasing temperature obeyed the Arrhenius equation with an activation energy of 123 kJ/mol. The linear regressions in Fig. 9 were used to calculate the reaction rate constants for various particle sizes ranging from 2.5 to 112.5 µm. In addition, the plot of $\ln k$ versus $\ln r$ in Fig. 12 shows that the constant n was calculated to be -0.78.

The conversion rate was controlled by the dissolution rate of cerium (IV) oxide as mentioned above. Therefore, the kinetics equation on the conversion of cerium (IV) oxide into cerium (IV) sulfate was $k = 2.55 \times 10^8 e^{-14800/T} C^{6.54} r^{-0.78}$.

4. Conclusion

The conversion of cerium (IV) oxide into cerium (IV) sulfate in sulfuric acid solutions was investigated. Cerium (IV) oxide was very slowly dissolved in acid solutions; it took more than 48 h to dissolve 0.02 mol cerium (IV) oxide powder with 2.5 µm average particle size completely in 100 ml sulfuric acid (8 mol/dm^3) at 125°C. The dissolved cerium cations exceeded the solubility and directly formed cerium (IV) sulfate. This result indicates that the conversion rate was controlled by the dissolution rate of cerium (IV) oxide.

Increases in sulfuric acid concentration and reaction temperature increased the dissolution rate of cerium (IV) oxide, whereas the increase in particle size decreased it. The initial amount of cerium (IV) oxide per sulfuric acid solutions (C/S) had no effect on the dissolution rate. In terms of the yield percentage of precipitated cerium (IV) sulfate after reaction equilibrium, increases in sulfuric acid concentration and C/S increased the yield percentage, whereas the particle size and the reaction temperature had no effect.

The kinetics data of cerium (IV) oxide dissolution fitted the shrinking core model with surface chemical reaction control well. This indicates that the calculated value of the activation energy in the dissolution of cerium (IV) oxide was 123 kJ/mol and the constants with respect to sulfuric acid concentration and particle size were 6.54 and -0.78, respectively. Since the conversion rate was controlled by the dissolution rate of cerium (IV) oxide, the rate constant of conversion of cerium (IV) oxide into cerium (IV) sulfate in acid solutions was expressed by the kinetics equation as $k = 2.55 \times 10^8 e^{-14800/T} C^{6.54} r^{-0.78}$.

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