

Unravelling NP-fertilizer production: intrinsic kinetics of phosphate ore digestion

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1. Introduction

Phosphate fertilizers are industrially produced via the digestion of phosphate ore with an acid, such as nitric acid. While the composition of the ore varies from one geographical location to another, phosphorous is always present as fluorapatite, i.e., $\text{Ca}_5(\text{PO}_4)_3\text{F}$ or $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$, which decomposes into phosphoric acid during the digestion [1-5]. At the typically employed operating conditions at the commercial scale, the digestion occurs in the so-called diffusion limited shrinking core regime [6]. In the present work, an attempt to determine the intrinsic kinetics of phosphate ore digestion by nitric acid is made by working with a significant excess of nitric acid while diluted in water.

2. Methods

The digestion of a phosphate ore with high P_2O_5 content, with 0.1-1.0 M nitric acid has been assessed in a 0.1 l batch reactor at temperatures ranging from 30 to 60°C. Evidence for the absence of external mass transfer limitations was found by obtaining identical digestion profiles by varying the stirring rate between 100 and 500 RPM (not shown). The progress of the reaction is followed by measuring the phosphate content of the samples taken at well-defined time intervals *via* UV/VIS measurements. The commercial Athena Visual Studio (AVS) software was used to perform the parameter estimation *via* regression.

3. Results and discussion

The results of the kinetic experiments of the phosphate ore digestion with nitric acid are shown in Figure 1, along with the corresponding model simulations and the parity diagram for the P_2O_5 conversion, as discussed below.

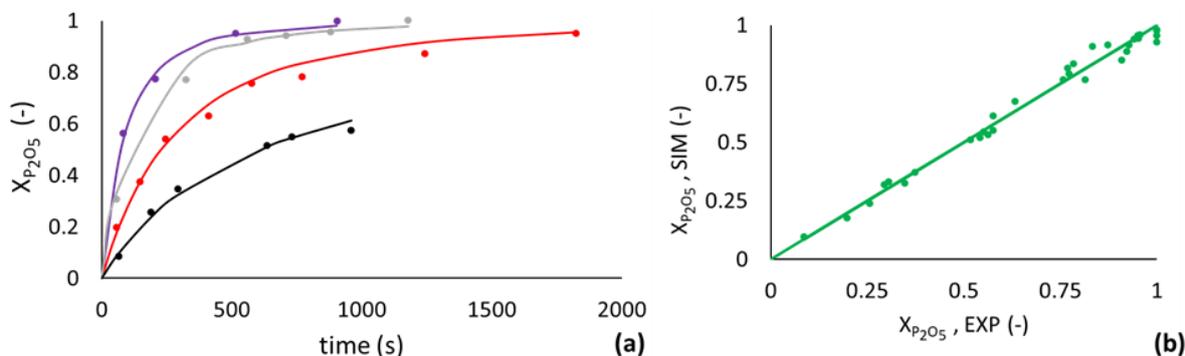


Figure 1. (a) P_2O_5 conversion as a function of batch time for the digestion of 400 mg phosphate ore with nitric acid in a 0.1 l batch reactor, the symbols represent the experimental observations while the lines represent the model simulated. Purple: $\text{CHNO}_3 = 1.0 \text{ M}$, $T = 60^\circ\text{C}$, Gray: $\text{CHNO}_3 = 1.0 \text{ M}$, $T = 50^\circ\text{C}$, red: $\text{CHNO}_3 = 1.0 \text{ M}$, $T = 30^\circ\text{C}$, black: $\text{CHNO}_3 = 0.1 \text{ M}$, $T = 60^\circ\text{C}$, (b) Parity diagram for the P_2O_5 conversion of the kinetic model for phosphate ore digestion with nitric acid.

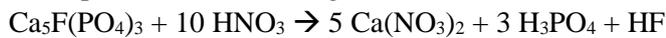
These experiments exhibit only a mild temperature dependence, while the digestion rate is significantly lower at more diluted conditions. Based on these observations a power law model (1) is proposed based on the diffusion limited shrinking core regime:

$$r = k C_{ore}^a C_{HNO_3}^b n_{ore}^{1/3} \quad [\text{mol mL}^{-3} \text{ s}^{-1}] \quad (1)$$

The last factor in equation (1) quantifies the shrinking of the particle as proportional to $n_{ore}^{1/3}$, given that the shrinking surface area dA/dr is proportional to r and the number of moles of phosphate ore is proportional to the volume of the particle, i.e. $n_{ore} \sim r^3$. The temperature dependence is accounted for using a reparametrized Arrhenius law as a function of the rate coefficient k_{Tmin} at the minimal temperature, $T_{min} = 30 \text{ }^\circ\text{C}$ (303 K), and the activation energy E_a as shown in equation (2):

$$k = k_{Tmin} \exp\left(-\frac{E_a}{R} \left(\frac{1}{T} - \frac{1}{T_{min}}\right)\right) \quad (2)$$

The net production rates R for the phosphate ore, nitric acid and phosphoric acid are calculated in correspondence with the digestion reaction:



$$R_{ore} = -r, \quad R_{HNO_3} = -10 r, \quad R_{H_3PO_4} = 3 r \quad [\text{mol mL}^{-3} \text{ s}^{-1}]$$

Thus, in total, 4 parameters (a , b , E_a , k_{Tmin}) are estimated for the digestion of phosphate ore, based on the minimization of the sum of squares using AVS, see Table 1.

Table 1. Parameter values and their 95% confidence intervals obtained after regression of the kinetic model of phosphate ore digestion with nitric acid to the experimental data

	estimated parameter value		units	estimated parameter value (dimensionless)		
k_{Tmin}	$1.1 \cdot 10^{-4}$	$\pm 8.0 \cdot 10^{-5}$	$\text{m}^{3(a+b-1)} \text{mol}^{-(a+b-2/3)} \text{s}^{-1}$	a	1.06	± 0.17
E_a	31.9	± 5.5	kJ mol^{-1}	b	0.83	± 0.08

Rate equation (1) allows to simulate the effect of temperature and nitric acid concentration accurately, see Figure 1 (a). This modelling effort shows that the intrinsic phosphate ore digestion kinetics depend on the nitric acid concentration with a partial reaction order amounting to 0.8, unlike what is typically reported for shrinking core kinetics [6]. The digestion kinetics also depend on the solid concentration, i.e. the ore, and, as can be seen from Table 1, this is a first order dependence. Thus, the total reaction order for the phosphate ore concentration is 4/3, 1 stemming for the chemical reaction and 1/3 stemming from the shrinking core effect. The activation energy amounts to 32 kJ mol^{-1} , as expected for a digestion reaction proceeding at temperatures as low as 30°C. The difference with literature values [2, 7], for varying solvents, can be explained by the absence of external mass transfer limitations in our work.

It can also be seen from Table 1 that all parameters are estimated significantly as zero is not included in the individual 95% confidence intervals. The regression is also globally significant with an F value amounting to 590, which sufficiently exceeds the tabulated value of 4.2. No significant correlation between the parameters was found as the maximum binary correlation coefficient remained below 0.95 .

4. Conclusions

The digestion of phosphate ores with nitric acid has been investigated experimentally as well as via kinetic model construction. The kinetic model allows describing the P_2O_5 conversion at various temperatures and initial nitric acid concentrations, ranging from 30 to 60°C and 0.1 – 1.0 M respectively. It was shown that the dependence of the digestion rate of the phosphate ore concentration is first order, originating from the chemical reaction, and an additional 1/3th order, stemming from particle shrinking. All model parameters were statistically significant without being correlated to each other.

References

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