



A sustainable process to utilize ferrous sulfate waste from titanium oxide industry by reductive decomposition reaction with pyrite



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ABSTRACT

Ferrous sulfate waste has become a bottleneck in the sustainable development of the titanium dioxide industry in China. In this study, we propose a new method for the reductive decomposition of ferrous sulfate waste using pyrite. Thermodynamics analysis, tubular reactor experiments, and kinetics analysis were performed to analyze the reaction process. The results of the thermodynamic simulation showed that the reaction process and products were different when molar ratio of $\text{FeSO}_4/\text{FeS}_2$ was changed. The suitable molar ratio of $\text{FeSO}_4/\text{FeS}_2$ was 8–12. The reaction temperature of ferrous sulfate with pyrite was 580–770 K and the main products were Fe_3O_4 and SO_2 . The simulation results agreed well with the experimental results. The desulphurization rate reached 98.55% and main solid products were Fe_3O_4 at 823.15 K when mole ratio of $\text{FeSO}_4/\text{FeS}_2$ was 8. Nano-sized magnetite was obtained at this condition. The kinetic model was investigated by isoconversional methods. The average E value was $244.34 \text{ kJ mol}^{-1}$. The ferrous sulfate decomposition process can be treated as autocatalytic reaction mechanism, which corresponded to the expanded Prout–Tompson (Bna) model. The reaction mechanism of autocatalytic reactions during the process of ferrous sulfate decomposition were explored, the products of Fe oxide substances are the catalytic components.

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1. Introduction

Ferrous sulfate is a solid industrial byproduct of titanium dioxide manufacture by the sulfate method and its main mineral component is $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$. In China, 98% of the titanium dioxide is manufactured using the sulfuric acid method, thereby producing over 7 million tons of ferrous sulfate waste each year, and the annual growth rate in waste emissions exceeds 10% as titanium dioxide production expands [1]. Most manufacturers store massive volumes of waste instead of preventing pollution due to the high costs of environmental protection. These huge volumes of ferrous sulfate cause severe pollution in the surrounding environment, but they are also a massive waste of sulfur and iron resources. Thus, ferrous sulfate is a major bottleneck in the sustainable development of the Chinese titanium dioxide industry because of pressure to improve environmental protection and other policies [2,3]. As a consequence, there is an urgent need to either dispose of or utilize this hazardous solid waste in an effective manner.

Several methods can be used to treat ferrous sulfate [4–6]. For example, Su et al. employed ferrous sulfate as a chemical reductant to treat hexavalent chromium during chromite ore processing, where Fe(II) was used to reduce Cr(VI) to Cr(III) [7]. Zouboulis et al. investigated the use of ferrous sulfate as a raw material in the preparation and application of polymeric sulfate, which can be employed as a water purifying agent [8]. Other reported uses of ferrous sulfate include the manufacture of iron oxide pigments and as a feed additive. However, all of these methods are limited because they only use the sulfur or iron resources specifically and they are restricted by their low market demand. Thus, the comprehensive utilization of sulfur and iron as resources to obtain additional value from an improved product remains a challenge. Roasting pyrite blended with ferrous sulfate to produce sulfur dioxide and iron oxide slag in an oxidizing atmosphere is a comprehensive method for utilizing ferrous sulfate, which has been studied in China since the 1980s. However, industrial implementations have not been promoted because the process still has several disadvantages, including the high concentration of SO_3 in the flue gas, which can corrode the equipment, while the high roasting temperature is difficult to control, and only a low ratio of ferrous sulfate can be added. Previously, our group studied ferric sulfate decomposition using pyrite, which successfully recovered sulfur

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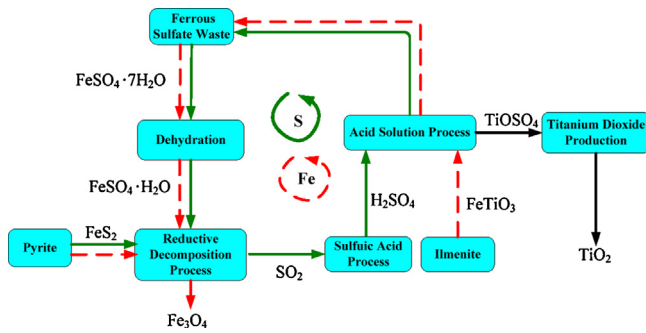


Fig. 1. Recycling sulfur and iron process of waste ferrous sulfate.

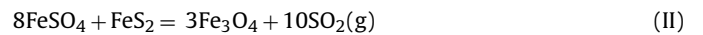
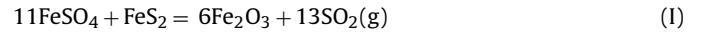
and iron resources from the waste, although the process is relatively complex because it involves an oxidation step. Thus, to facilitate the better recovery of sulfur and iron resources from waste, we propose an improved waste treatment process (Fig. 1), where ferrous sulfate is decomposed reductively by pyrite to produce iron oxide and sulfur dioxide in nitrogen or a reducing atmosphere. In the present study, thermodynamics and phase diagram calculations were undertaken to predict the possible decomposition reactions

between ferrous sulfate and pyrite and its products. Experimental data were adopted to elucidate the reaction mechanism and reaction conditions. The raw material and products were examined using X-ray diffraction (XRD) and Scanning electron microscopy (SEM). A kinetic model for the decomposition reaction was proposed and used to interpret the experimental data.

2. Theoretical basis

2.1. Thermodynamic analysis

The net reaction equations for the decomposition of ferrous sulfate by pyrite are as follows:



Factsage 6.1 software was used to calculate phase diagram and the equilibrium compositions of the reaction system were simulated by HSC Chemistry software [9]. The criterion used for the simulation was the minimization of the Gibbs free energy according to two hypotheses. The first hypothesis was that all of the input substances were considered to be ideal substances, and two or multiple substances were assumed to be completely mixed when they

Table 1
Thermodynamic properties of pure phases used in the simulation.

Species	Temperature range (K)	Enthalpy H^a (kJ mol ⁻¹)	Entropy S^b (J mol ⁻¹ K ⁻¹)	Coefficients of C_p^c			
				A	B	C	D
FeSO ₄ (s)	298.15–500	–928.848	120.959	202.581	–296.367	–40.839	363.381
	500–900			101.395	105.037	–32.274	–48.376
S ₂ (g)	298.15–2000	128.600	228.164	34.671	3.286	–2.816	–0.312
SO ₂ (g)	298.15–500	–296.813	248.220	29.134	37.222	0.058	–2.885
	500–2000			54.779	3.350	–24.745	–0.241
Fe ₂ O ₃ (s)	298.15–700	–823.000	87.400	143.566	–36.323	–31.433	71.792
	700–950			637.809	–963.532	–447.383	560.951
Fe ₃ O ₄ (s)	298.15–850	1118.383	146.147	475.215	–873.665	–120.520	800.730
	850–1870			49.827	72.534	855.536	0.000
FeS (s)	298.15–411	–101.671	60.321	–273.270	779.182	81.241	0.000
	411–598			72.358	0.000	0.000	0.000
	598–1465			94.584	–83.667	1.410	47.944
FeS ₂ (s)	298.15–1500	–170.300	52.930	72.387	8.850	–11.428	0.001
Fe ₂ S ₃ (s)	298.15–398	–280.002	152.289	47.798	0.000	0.000	0.000
FeO (s)	298.15–600	–267.27	57.59	50.278	3.651	–1.941	8.234
	600–900			30.849	46.228	11.694	–19.278
Fe ₇ S ₈ (s)	298.15–398	–736.384	485.762	398.568	0.000	0.000	0.000

^a Standard molar formation enthalpy, standard state is at $T=298.15$ K.

^b Standard entropy of the substance, standard state is at $T=298.15$ K.

^c Coefficients of molar heat capacity under constant pressure.

Table 2
Reaction types and corresponding reaction equations of 16 different models.

Code	$f(\alpha)$	Reaction type
F1	$1 - \alpha$	First-order reaction
F2	$(1 - \alpha)^2$	Second-order reaction
F _n	$(1 - \alpha)^n$	n th-order reaction
R2	$2(1 - \alpha)^{1/2}$	Two-dimensional phase boundary reaction
R3	$3(1 - \alpha)^{2/3}$	Three-dimensional phase boundary reaction
D1	$1/2\alpha$	One-dimensional diffusion
D2	$[-\ln(1 - \alpha)]^{-1}$	Two-dimensional diffusion
D3	$3/2(1 - \alpha)^{2/3}[1 - (1 - \alpha)^{1/3}]^{-1}$	Three-dimensional diffusion (Jander's type)
D4	$3/2[(1 - \alpha)^{1/3} - 1]^{-1}$	Three-dimensional diffusion
B1	$\alpha(1 - \alpha)$	Prout–Tompkins equation
B _n a	$\alpha^n(1 - \alpha)^m$	Prout–Tompkins equation, n -order auto-catalysis
C1	$(1 - \alpha)(1 + K_{\text{cat}}\alpha)$	First-order reaction with auto-catalysis
C _n	$(1 - \alpha)^n(1 + K_{\text{cat}}\alpha)$	n -Order reaction with auto-catalysis
A2	$2(1 - \alpha)[- \ln(1 - \alpha)]^{1/2}$	Two-dimensional nucleation
A3	$3(1 - \alpha)[- \ln(1 - \alpha)]^{2/3}$	Three-dimensional nucleation
A _n	$n(1 - \alpha)[- \ln(1 - \alpha)]^{(n-1)/n}$	n -Dimensional nucleation/nucleus growth according to Avrami/Erofeev

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