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Kinetic analysis of retention of SO_2 using waste ulexite ore in an aqueous medium

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ABSTRACT

This study was carried out under atmospheric pressure and examined the kinetics of retention of SO_2, a toxic gas, by waste ulexite ore (*WUO*) from a boron concentration plant, as well as the kinetics of passing B_2O_3 content of *WUO* to solution.

The parameters of temperature, solid-to-liquid ratio, particle size, gas flow rate, and stirring speed were selected for the experiments carried out in a jacketted cylindirical glass reactor. The data on retention-dissolution and an XRD graph showed that SO_2 had been captured as $CaSO_3{\cdot}0.5H_2O$, and that the B_2O_3 content of *WUO* had almost completely passed into the aqueous medium.

A kinetic evaluation, performed with the retention-dissolution data using kinetic models for heterogenous reactions, found that the kinetics model for SO_2 retention fitted diffusion through product layer control. In addition, the kinetics model for the B_2O_3 dissolution fitted the diffusion through product film control. Activation energies for SO_2 retention in solid waste and B_2O_3 dissolution were 6196 J mol^{-1} and 15436 J mol^{-1} respectively.

1. Introduction

The most important reasons for atmospherical changes in the last 200 years are the anthropogenic effects such as fossil fuel consumption for energy production and extermination of forests, despite volcanic activity and another natural factors [1]. Large amounts of SO_2, NOx, and CO_2 are emitted into the atmosphere by burning fossil fuels. The most important fraction of sulphur oxides that stem from burning sulphurous fuels is SO_2, which is emitted by industrial activities such as roasting of sulphurous ores. All these activities cause of global warming [2].

Recently, SO_2 has been determined to be the most important contaminant gas emitted by burning fossil fuels. Various forms of sulphur in fossil fuels is converted to SO_2 when burned; and it has harmful effects on both living and non-living things. SO_2 produces sulphuric acid by combining with steam and oxygen in the atmosphere, resulting in acid rain that kills plants, destroys forests and the natural structure of soil, and ruins water resourses. These rains damaged historical buildings in the age of industrialization before environmental consciousness has been raised in Europe [3]. SO_2 causes acute respiratory tract illnesses when it exceeds certain concentrations and attacks plants and machinery [4].

The emission of SO_2 to the atmosphere can be prevented in two ways; desulphurization of coal before firing or desulphurization of flue gas after firing. In the former way, sulphur content of coal is removed by physical and chemical methods. Some studies about desulphurization of flue gas are cited below [5–7].

A study, carried out to prevent emission of flue gases to the environment and to determine the ideal conditions for coke production from coal, used the SO_2 content of flue gases in the activation process during coke production, and showed that flue gas can be used for this purpose [8]. Another study of SO_2 removal by fabric filters showed that input SO_2 concentration did not have an important effect on removal yield; that an increase in flue gas temperature increased SO_2 removal yield in the fabric filters; and that relative humidity had an important effect on removal yield [9]. A study on the parameters that affect SO_2 removal from flue gases using active carbons with various structural and chemical properties determined that particle size had an important effect on removal yield; and that phenols and lactone groups seen in FTIR analysis of active carbons also affected SO_2 removal [10].

Macias-Perez et al examined the parameters that affect the retention of SO_2 on CaO /active carbon sorbents, selecting the parameters of the

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Nomenclature

X	Fractional conversion
t	Reaction time (min)
T	Reaction temperature, (K)
D	Mean particle size (µm), arithmetical average of upper and lower sieve sizes
G	Gas flow rate ($\mathrm{mL\,min^{-1}}$)
R	Gas constant ($8.314\,\mathrm{J\,mol^{-1}\,K^{-1}}$)
r^2	Regression coefficient
k	Reaction rate constant
E	Activation energy ($\mathrm{J\,mol^{-1}}$)
A	Frequency factor
S/L	Solid to liquid ratio

Subscripts

g	Gas
s	Solid
aq	Aqueous Solution

reaction time, SO_2 partial pressure, CaO amount, and O_2 amount. In another study by Macias-Perez et al., the authors found that O_2 presence in the gas mixture did not affect SO_2 removal yield [11]. A study analyzed the effects of the flue gas components on the reaction between $Ca(OH)_2$ and SO_2 in a differential fixed-bed reactor under the similar conditions to the bag filters of a spray-drying flue gas desulfurization system, and found that the presence of H_2O, CO_2, NO_X, and O_2 in the flue gas was useful for the reaction between $Ca(OH)_2$ and SO_2, in order to capture the SO_2 during the low-temperature dry and semidry flue gas desulfurization processes [12]. A MCM-41 sorbent with two metal oxides (CuO, CeO_2) and an alkaline additive ($LiCl$) was used to remove SO_2 from gas streams at 673 K [13].

Wet flue gas desulphurization processes are those most preferred processes by business enterprises due to high SO_2 recovery, ease of applicability of adsorbents, and no need for more knowledge about process management [14–17]. Although the systems in which the active substance is discharged after retaining SO_2 are generally regarded as low-cost, removal of mold or dry waste carried by these systems poses a problem. Therefore, it is important to develop systems by which waste products are evaluated or the active substance is recovered at a low cost.

Turkey has the 73% of the world's boron reserves with boron ores such as colemanite ($2CaO{\cdot}3B_2O_3{\cdot}5H_2O$), ulexite ($Na_2O{\cdot}2CaO{\cdot}5B_2O_3{\cdot}16H_2O$), and tincal ($Na_2B_4O_7{\cdot}10H_2O$). All of these mines have simple treatment plants on site, where concentrates of tincal, colemanite and ulexite are produced in various grades and fractions.

Many studies exist on the dissolution of concentrated boron ores with SO_2 in aqueous media [18–20].

During ore treatment and refining, which produce boron concentrates and refined boron products of high chemical purity, a substantial amount (~400,000 tons/y) and various types of solid boron-containing wastes are formed and rejected in tailing dams or discharged to landfill [21]. In Bigadiç, Turkey, ulexite is mined with the colemanite from ore deposits; the colemanite and ulexite are seperated as concentrated colemanite and concentrated ulexite. The amount of waste ulexite ore (WUO), called as "−3 mm under the sieve," is about 5000 tons/y and cannot be evaluated. Ulexite in WUO can dissolve to some degree in rain or snow water, causing contamination of the soil and water reserves; WUO must therefore be eliminated and/or treated appropriately [22].

Various desulphurization methods have been attempted so far; however, WUO with basic components have not been used in retention of SO_2. The present study examined the kinetics of SO_2 gas retention using WUO. The hypothesis was that SO_2 retention as $CaSO_3\cdot 0.\ 5H_2O$ with CaO in WUO, which causes environmental pollution, is an acceptable alternative method due to easy applicability and contribution to environmental protection. Therefore, kinetic models for WUO dissolution and SO_2 retention was studied: the WUO was evaluated and SO_2 was removed by being retained as $CaSO_3\cdot 0.5H_2O$.

2. Materials and methods

2.1. Materials

The WUO used in experiments was provided by the Eti Mine Corporation of Bigadiç, Turkey. Sulphur dioxide gas was provided by the Habaş Corporation (Turkey). The ore sample was ground using a laboratory grinder and separated into fractions with ASTM standard sieves. Table 1 shows these fractions and their contents. The XRD pattern of the original sample showed that WUO included ulexite ($Na_2O{\cdot}2CaO{\cdot}5B_2O_3\ {\cdot}16H_2O$), colemanite ($2CaO{\cdot}3B_2O_3{\cdot}5H_2O$) and calcite ($CaCO_3$), but did not identify the clay minerals (Fig. 1). WUO collected from the waste landfill in different bags was thoroughly blended before being divided and re-packed into 20–25 kg sample bags. Chemical analysis showed that the WUO contained 37% ulexite, 18% colemanite, 35% carbonate minerals and 10% clay minerals.

2.2. Experimental procedure

The dissolution experiments were carried out in a spherical glass reactor of 250 ml volume fitted with a mechanical stirrer, gas sparger system, and a refluxed condenser open to the atmosphere. The atmospheric condition was around 610 mmHg and 294 K in the lab. The reactor was put in a temperature controlled water bath. The reactor was filled with 150 ml water, which was saturated by SO_2 gas with a fixed flow rate through the sparging system while stirring at a predetermined speed. Once the desired temperature was reached, a sufficient amount of WUO was quickly added into the reactor to yield a certain S/L ratio. During the reaction, the reactor temperature was kept constant at the determined temperature. The SO_2 gas was passed through concentrated H_2SO_4 to dry, and then through a coke column to retain acid residues before being sent to a flowmeter. Also, the SO_2 gas flow through the reactor was kept constant throughout the reaction period. Fig. 2 shows the experimental setup, and Table 2 shows the experimental parameters and theirs levels.

The pH of the reactor content was continuously measured and recorded during the experiments. At the end of the reaction period, the content of the reactor was filtered and solid washed at the room temperature.

Filtrate was then analyzed for B_2O_3, Na^{+}, Ca^{2+}, Mg^{2+}, SO_3^{2-} and SO_4^{2-} : a volumetrical method was used for B_2O_3 [23], an atomic

Table 1
The fractions of waste ulexite ore and their chemical compozitions.

Fractions (µm)	Components(%)						
	B_2O_3	Na_2O	CaO	MgO	C	DL[a]	IMA[b]
−600 + 355	23.18	2.43	26.92	4.75	3.93	37.11	8.76
−355 + 250	24.52	2.82	27.21	4.23	3.54	34.48	7.42
−250 + 180	25.24	3.30	23.72	4.19	3.04	34.08	7.76
−180 + 150	27.59	3.70	24.00	4.45	2.83	33.30	7.92

[a] DL:Driying Loss.

[b] IMA:Insoluble matter in acid.