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Mixed waste ferrite as a novel sorbent for carbon dioxide derived from flue gases

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Ferrite is a potential sorbent for flue gases such as CO_2, H_2S and SO_2. This paper discusses the adsorption and decomposition of CO_2 into carbon by hydrogen-activated waste ferrites prepared from Berkeley Pit acid mine water (Butte, MT). The decomposition effectiveness of these waste ferrites was studied at 300 °C and compared with the synthetic magnetite obtained from ferrous sulfate solution in our laboratory. The decomposition was measured by two methods: indirectly by measuring the adsorption rate of CO_2 and directly by analysing the carbon deposited on the samples. The results indicated that the mixed waste ferrite had good affinity for the adsorption and decomposition. The CO_2 decomposition data of both sorbents fitted the first-order reaction kinetics. Even though the surface area of the magnetite was higher than that of waste ferrite, the CO_2 decomposition rate of the waste ferrite was estimated to be 2.5 times higher than that of magnetite under identical conditions. The carbon analysis deposited on the sample indicated that the CO_2 was 100% decomposed into carbon and other carbon/hydrogen compounds by the waste ferrite, whereas the conversion was 43% by the magnetite. In terms of specific adsorption of carbon, ferrite was three to five times more efficient than magnetite.

1. Introduction

Coal-derived flue gases which contain $CO_2/SO_2/NO_x/H_2S$ produce large environmental problems such as global warming and acid rain. Metal oxides have been traditionally used as sorbents to clean the coal-derived flue gases. Examples are MgO, ZnO, CuO and lime-based sorbents. Recently, a special class of ferrites was shown to be very effective sorbents for H_2S and CO_2. Tamaura and Tabata [1] reported that the activated magnetite obtained by the hydrogen reduction could decompose CO_2 gas into carbon with almost nearly 100% efficiency at 290 °C. During the reaction, the oxygen atoms of adsorbed CO_2 molecules are incorporated into the oxygen-deficient site of the activated magnetite, and the carbon is deposited on the solid surface to form elementary and/or polymerized carbon. The authors reported that the reaction did not change the original spinel-type crystal structure of the materials. Several single metal-bearing ferrites (such as zinc ferrite, manganese ferrite, etc.) having spinel crystal structure, such as magnetite, have also been used in the CO_2 decomposition studies [2–5].

It could therefore be anticipated that if the mixed ferrites were prepared from a waste solution containing several metal ions (copper, magnesium, zinc, calcium, etc.), the simultaneous presence of several metals in the ferrite structure could probably induce some synergetic effect and enhance the adsorption. The objective of this study was to test this hypothesis. The mixed waste ferrite was prepared from the heavy-metal contaminated Berkeley Pit acid mine water and used as sorbent in the decomposition study of the CO_2.

2. Experimental procedure

2.1. Sorbents

Two sorbents were used in this study: the magnetite and the mixed waste ferrite. The magnetite was prepared from the pure ferrous sulfate solution. The mixed waste ferrite was prepared from the Berkeley Pit acid mine water. Table I lists the composition of the Berkeley Pit acid mine water (influent) and the treated water (effluent).

Both sorbents were prepared by the same technique, i.e. by controlled air oxidation followed by ageing at room temperature, reported in our previous research work [6–8]. Research-grade H_2 and CO_2 gases were used.

2.2. Synthesis

22.5 g $FeSO_4 \cdot 7H_2O$ was added to 500 ml distilled water for the magnetite synthesis. A similar amount of ferrous sulfate was added to 500 ml Berkeley Pit acid mine water for the mixed waste ferrite synthesis. 4 M NaOH solution was added to adjust the pH of the solution at 10.5. The suspension was oxidized for 15 min in the case of magnetite and 20 min in the case of waste ferrite by sparging air. This was followed by a 2 day ageing of formed precipitates at room temperature. The precipitates were filtered, dried in air and

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TABLE I Concentration of heavy metals in Berkeley Pit water and treated water

Elements	Concentration of heavy metals (p.p.m.)	
	Berkeley Pit water	Treated water
Fe	439	< 0.1
Zn	607	< 0.1
Mn	223	< 0.1
Al	334	0.9
Cd	3.1	< 0.1
Cu	186	< 0.1
Mg	497	13.7
Ca	270	126

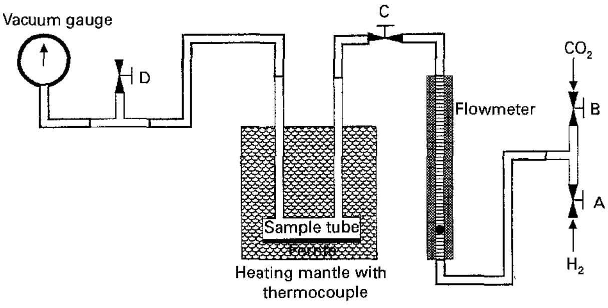

Figure 1 Schematic diagram of CO_2 decomposition with activated magnetite.

magnetically separated. The BET adsorption surface area of the magnetite and mixed waste ferrite was measured to be 56 and 38 $m^2 g^{-1}$, respectively.

2.3. Activation

Both sorbents were first reduced by hydrogen in the apparatus as shown in Fig. 1. The hydrogen-reduction step was aimed to make the sorbents "oxygen deficient". 0.5 g material was placed in the sample tube having 6 ml volume. The tube was heated to 300 °C in the heating mantle. Valves A, C and D were open and valve B was closed. Hydrogen gas was passed through the packed bed of material for a predetermined time (ranging from 1–3 h).

2.4. Decomposition

After the sample had reduced for a given time, valve A was closed and valve B was opened for about 5 min to allow the CO_2 to replace H_2 in the reaction tube. Because most of the gas in the reaction tube was CO_2, it was reasonable to assume the partial pressure of CO_2 to be proportional to the inner pressure of reaction cell [1]. In this way, the relative amount of CO_2 present at any time in the tube could be simply measured by measuring the inner pressure of the reaction tube. The inner pressure was measured by the vacuum gauge mounted on the reaction tube. The pressure measurement was done after closing valves C and D. The largest vacuum attained in the tube was 350 mm Hg. The relative amount of CO_2 in the reaction tube was calculated using $(1 - p/350)$ where p was the vacuum measured of the reaction tube. The carbon deposited on the solid sample was analysed by the carbon elemental analyser (Perkin–Elmer 2400 Series II CHNS/O analyser). X-ray diffraction and Fourier transform–infra red (FT–IR) analysis was carried out on the activated and carbon-adsorbed sorbents.

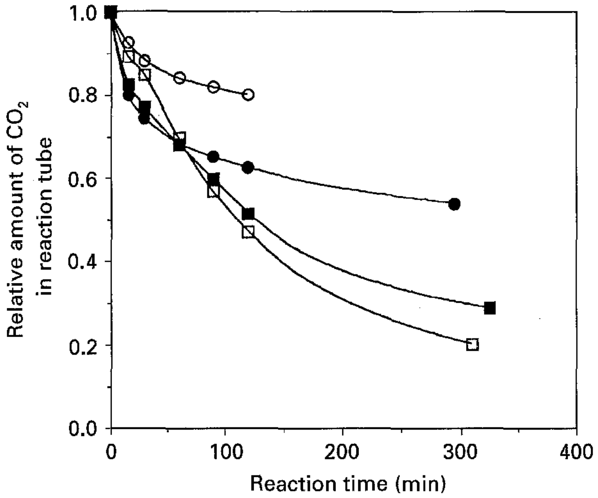

Figure 2 Effect of reaction time on the relative amount of CO_2 in the reaction tube by using magnetite activated for different times: (○) 0, (●) 1 h, (□) 2 h, (■) 3 h.

3. Results and discussion

3.1. Effect of activation time

Fig. 2 shows the effect of H_2 activation time on the relative amount of CO_2 present in the reaction tube containing magnetite. Magnetite powder was activated at 300 °C for three different time periods: 1, 2 and 3 h. It is clear from the plot that the magnetite with no activation had a very little CO_2 decomposition capability. It was interesting to note that the larger activation time favoured higher CO_2 decomposition. However, the activation time beyond a limiting value caused the CO_2 decomposition to be adversely affected. This is evident from Fig. 2. The amount of CO_2 decomposed after 3 h activation is smaller than the amount after 2 h. This is probably attributed to the magnetite changing to other iron oxides and/or coalescence of particles [9]. Another possible explanation is that the excess oxygen taken out during activation [1] may cause the activated magnetite to react with CO_2 to form stable magnetite. The following reactions might take place

$$Fe_3O_4 + \delta H_2 \rightarrow Fe_3O_{4-\delta} + \delta H_2O \quad (1)$$

$$Fe_3O_{4-\delta} + \delta/2CO_2 \rightarrow Fe_3O_4 + \delta/2C \quad (2)$$

Therefore, the control of activation period is important for the purpose of attaining good CO_2 decomposition capability. In this study, 2 h activation time was considered to be the optimum.

3.2. Decomposition extent by carbon analysis

Fig. 3 shows the comparative results of CO_2 decomposition obtained using the magnetite and mixed

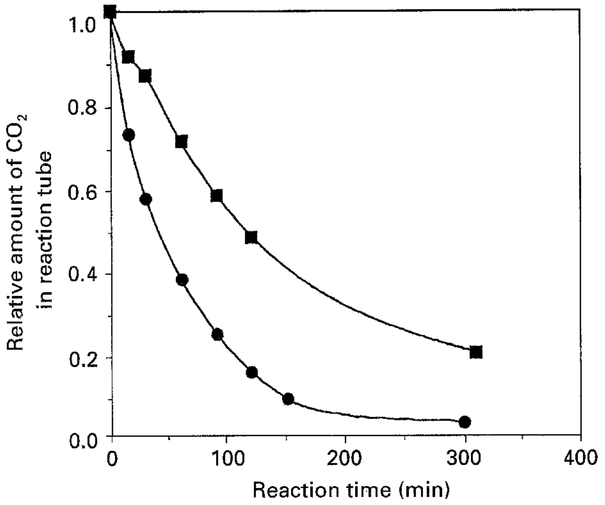

Figure 3 Effect of reaction time on the relative amount of CO_2 in the reaction tube: (■) magnetite, (●) mixed ferrite.

waste ferrite. Both sorbents were activated for 2 h under identical conditions. The decomposition test was run until the highest vacuum condition was attained in the reaction tube. The carbon deposited on the magnetite and mixed waste ferrite was analysed to be 0.061 and 0.191 (wt %), respectively. The corresponding weight of adsorbed carbon was 0.305 and 0.955 mg. Specific adsorption was calculated to be 0.0109 and 0.0503 mg m^{-2} (considering the total surface area of materials present in the reaction tube to be 0.5 A, where A is the specific surface area of materials in $m^2 gm^{-1}$ ($A_{magnetite} = 56\ m^2\ g^{-1}$ and $A_{mixed\ ferrite} = 38\ m^2 g^{-1}$)). Note that even though magnetite was finer, the specific adsorption of carbon on mixed waste ferrite was about five times than that of magnetite. Assuming the CO_2 to be an ideal gas and the vacuum generated was entirely due to CO_2 decomposition into carbon, the weight of initial carbon to be decomposed in the reaction system can be calculated from $W = 12n = 12PV/RT$, where $P = 350/760$ atm, $V = 6 \times 10^{-3}$ l, $R = 0.082$ l, atm $K^{-1} mol^{-1}$ and $T = 573$ K. The theoretical weight of carbon on the sorbent would, therefore, not exceed 0.706 mg. This indicates that, in the case of mixed waste ferrite, carbon was already present in the feed material. It is possible that Berkeley Pit acid mine water contains dissolved carbon. This discrepancy has to be verified by the pending carbon analysis of the feed sorbents which will determine precisely the extent of decomposition. Suffice to say that the mixed waste ferrite was able to decompose CO_2 into carbon more effectively (100%) than the magnetite (43%).

3.3. Kinetic analysis

From the standpoint of kinetics, the mixed waste ferrite was also superior. If we define $X = p/350$ to be the fraction of CO_2 decomposed in the reaction tube, and consider the CO_2 decomposition into carbon to be the first-order reaction, the plot of $\ln[1/(1 - X)]$ versus time must be a straight line. It was interesting to note that the experimental data indeed fitted the first-order rate law as shown in Fig. 4. Mathematically

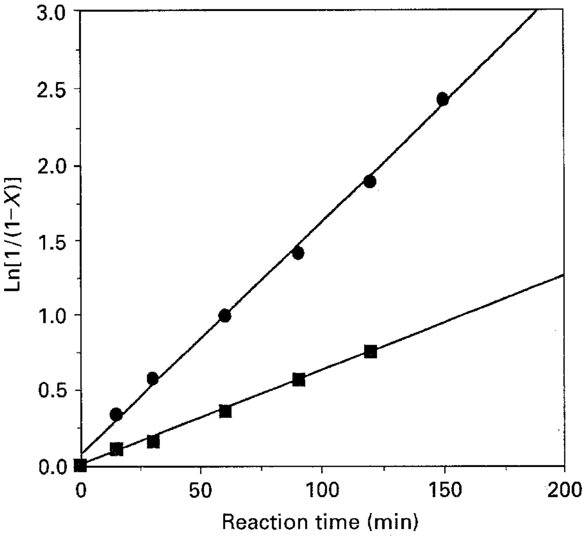

Figure 4 First-order plots of CO_2 decomposed to carbon. (●) Mixed ferrite, $\ln[1/(1 - X)] = 0.0155\,t$; (■) magnetite, $\ln[1/(1 - X)] = 0.00025\,t$.

$$dX/dt = -kX \tag{3}$$

$$\ln[1/(1 - X)] = kt \tag{4}$$

Quantitatively, the estimated rate of CO_2 decompositon by the mixed waste ferrite was about 2.5 times higher than that of the magnetite.

3.4. Decomposition extent by adsorption analysis

The specific adsorption (carbon deposited per unit surface area of sorbent) was calculated from the adsorption data and plotted in Fig. 5. It was interesting to note that the equilibrium carbon deposition amount on the mixed waste ferrite was about three times higher than that of magnetite. This may be attributed to the simultaneous presence of several divalent metal ions in the ferrite structure which makes the crystal lattice of mixed waste ferrite defective, thereby making it more reactive. The reaction mechanism is shown in Fig. 6. During hydrogen activation, the oxygen atom on the surface of the sorbent reacts with hydrogen to form water vapour, resulting in an "oxygen-deficient" or "cation-excess" structure. During CO_2 decomposition, CO_2 is first adsorbed on the surface and then the oxygen-deficient particle reacts with the oxygen of CO_2 to form normal magnetite or mixed waste ferrite and elementary carbon. Although regeneration studies of these sorbents have not been carried out so far, it is conceivable that the deposition of carbon on the sorbent could be used to generate methane, thereby regenerating the sorbents.

3.5. X-ray diffraction analysis

The magnetite and mixed waste ferrite samples before and after the reactions were analysed by X-ray powder diffraction method using CuK_α radiation. Table II shows the results of X-ray diffraction. It is clear that

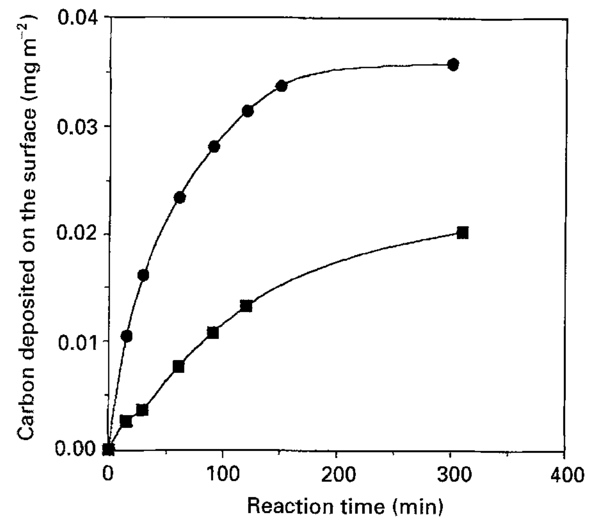

Figure 5 Effect of reaction time on the carbon deposited on the surface of (■) magnetite or (●) mixed ferrite.

the decomposition reactions do not alter the spinel structure of sorbents. There was slight decrease in 2θ angles and relative intensity, I/I_0 after the reactions. This may be attributed to the carbon attaching to the ions in the spinel structure which causes the lattice constants to increase.

3.6. FT–IR analysis

The mixed waste ferrite samples before and after the reactions were analysed by FT–IR. Fig. 7 shows the spectra of the powders. Fig. 7a is the spectrum of mixed waste ferrite prior to the reactions and the Fig. 7b is the spectrum of the reacted mixed waste ferrite. The wave numbers corresponding to the intensity peaks revealed the presence of carbon in the form of carboxylate and aliphatic functional groups.

4. Conclusions

1. Mixed waste ferrite prepared from the Berkeley Pit acid mine water in its activated state decomposed CO_2 into carbon with almost 100% efficiency, whereas the synthetic magnetite in its activated state was only 43% efficient.
2. The CO_2 decomposition rate by mixed waste ferrite was 0.015 min^{-1} which is 2.5 times higher than that of pure magnetite (0.006 min^{-1}).
3. The decomposition reaction mechanism for both the sorbents, however, was found to follow first-order reaction kinetics.
4. Even though magnetite was finer (58 m^2 g^{-1}) than mixed waste ferrite (38 m^2 g^{-1}), the specific adsorption of carbon on the ferrite was in the range of three to five times higher than that of magnetite.
5. The decomposition reaction did not change the original crystal structure of the sorbents.
6. The carbon deposited on the mixed waste ferrite was found to be in the form of carboxylate and aliphatic functional groups.
7. The preliminary study indicates that it is feasible to use mixed waste ferrites as potential sorbents for SO_2, H_2S and CO_2, major contaminants present in coal-flue gases.

Future work will be done to determine the effectiveness of the mixed waste ferrite to decompose SO_2 and H_2S separately. Subsequently, a mixture of gases (CO_2, SO_2 and H_2S) will be tested.

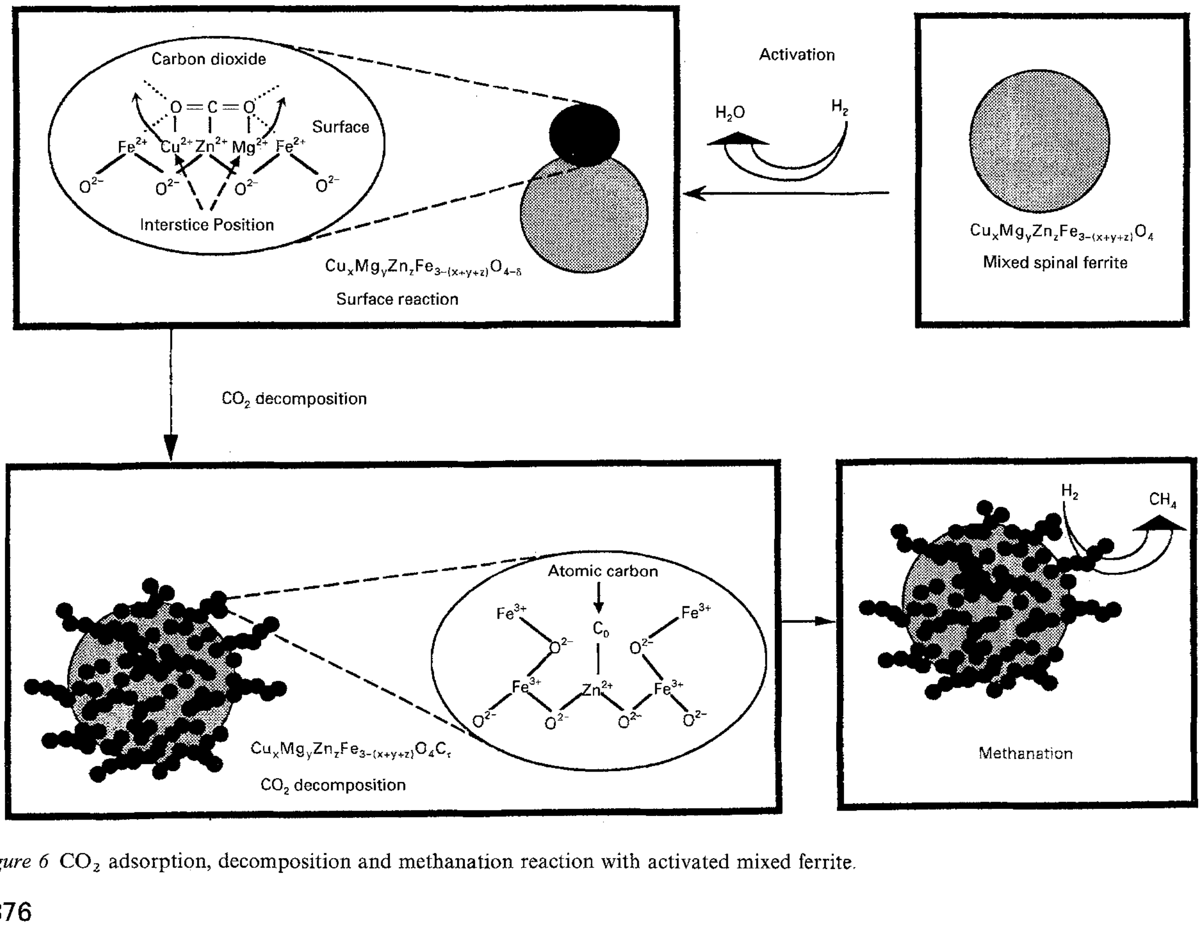

Figure 6 CO_2 adsorption, decomposition and methanation reaction with activated mixed ferrite.

TABLE II XRD data of the solid phases of magnetite and waste ferrite before and after the reactions at 300 °C

	$(h\,k\,l)$	Before		After	
		2θ (deg)	I/I_0	2θ (deg)	I/I_0
Magnetite	(2 2 0)	30.27	0.41	30.23	0.31
	(3 1 1)	35.62	1	35.60	1
	(4 0 0)	43.22	0.39	43.19	0.24
Ferrite	(2 2 0)	30.20	0.43	30.15	0.38
	(3 1 1)	35.57	1	35.54	1
	(4 0 0)	43.21	0.29	43.14	0.27

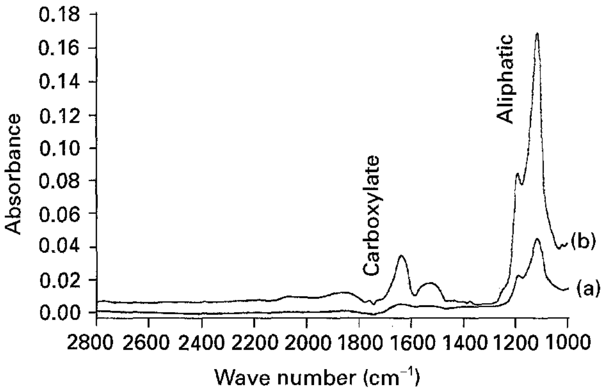

Figure 7 FT–IR spectra of mixed ferrite (a) before and (b) after the reactions.

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