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Effects of a CO$_2$ Pressure Process on the Solubilities of Major and Trace Elements in Oil Shale Solid Wastes

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■ Processing of oil shale at high temperatures produces a highly alkaline solid waste. The waste can be stabilized by a recarbonation process. In order to test a method for accelerating the recarbonation process, we exposed three moist oil shale solid waste (OSSW) samples to 5 psi CO$_2$ pressure for 1 h. The treated and untreated samples were equilibrated with water for 7 days and the chemical composition of the aqueous extracts determined. Before CO$_2$ treatment, the Ca^{2+} and Mg^{2+} concentrations appeared to be controlled by silicate phases present in the waste such as wollastonite (CaSiO$_3$), forsterite (Mg$_2$SiO$_4$), and talc (Mg$_3$Si$_4$O$_{10}$(OH)$_2$), which buffered the pH at ~12.0. The CO$_2$ treatment lowered the pH from 12.0 to ~9.0 through the formation of calcite. The Ca^{2+} concentrations from CO$_2$-treated samples suggested a close approach to saturation with respect to calcite (CaCO$_3$) whereas the Mg^{2+} concentrations appeared to be controlled by either magnesite (MgCO$_3$) or possibly a silicate. The CO$_2$ treatment generally decreased F and Mo concentrations in aqueous extracts. The F$^-$ concentration before and after CO$_2$ treatment appeared to be controlled by fluorite (CaF$_2$). Our results demonstrate that the CO$_2$ pressure process is an effective means of reducing the pH and the concentrations of F and Mo in aqueous extracts from alkaline solid wastes.

Introduction

Oil shale contains mainly kerogen and carbonate minerals. Oil is recovered from the oil shale by thermally degrading the kerogen at elevated temperatures, which results in production of large amounts of oil shale solid wastes (OSSW). These solid wastes are often alkaline (typical slurry pH may range from 10.0 to 13.0) and often contain elevated levels of toxic elements.

Reclamation of OSSW is often affected by the high pH and high solubilities of toxic elements. In addition, soluble toxic elements may leach from the disposal environment and migrate to groundwater (1–8).

During the processing of oil shale, high temperatures drive off CO$_2$ from carbonate minerals resulting in the formation of oxide and silicate phases. These phases react rapidly with water, and as a result, the pH of aqueous extracts of OSSW approach 12.0, and this affects the solubility relationships of many elements. The high pH increases the solubility and mobility of anionic trace elements, e.g., As, B, F, Mo, and Se (1–6). Among these trace elements, F and, to some extent, Mo have shown considerable mobility in OSSW disposal environments (4).

The high pH of OSSW decreases slowly as the CO$_2$-deficient materials absorb CO$_2$ from the atmosphere (recarbonation). However, natural recarbonation of OSSW occurs slowly, and this may hinder reclamation efforts intended to minimize potential pollution of natural resources (land/water) associated with the disposal of these materials.

The objectives of the research were as follows: (1) to investigate a process for accelerating the recarbonation process by reacting moist oil shale wastes under CO$_2$ pressure; (2) to examine the effects of CO$_2$ pressure treatment on the pH and solubilities of major (e.g., Ca and Mg) and trace (e.g., F and Mo) elements in aqueous extracts.

Materials and Methods

The samples used in this study were Western Reference Green River Formation oil shale from the Piceance Creek Basin in Colorado, which had been processed at 770, 1000, and 1295 K to produce PP3, Lurgi, and PP6 oil shale solid wastes, respectively. More details regarding the processing conditions are reported in Merriam et al. (9) and Nowacki (10).

Samples were ground to pass a 0.25-mm sieve to enhance the recarbonation process. However, under oil shale processing conditions samples may vary in particle size. For CO$_2$ pressure treatment experiments, a pressure vessel was designed (Figure 1) to react oil shale solid waste samples. The reaction vessel consisted of 30 cm by 30 cm polyvinyl chloride (PVC) cylinder with an o-ring seal lid and a pressure release valve to control the internal pressure. A stainless steel screen covered with filter paper was placed in the middle of the reaction vessel to hold samples. The gas inlet of the reaction vessel was connected to a CO$_2$ tank through a distilled H$_2$O flask to saturate the CO$_2$ with H$_2$O.

Fifty grams of each sample containing 15–20% moisture was spread over the filter paper. Before the gas outlet was connected to the pressure gauge, CO$_2$ from a gas tank was bubbled through distilled H$_2$O, using a sparger, to purge the initial air from the reaction vessel. Approximately 5 psi pressure was maintained inside the reaction vessel. After a reaction period of 1 h, the sample was removed and sufficient distilled H$_2$O was added to the sample to prepare a saturated paste. The saturated paste was immediately measured for pH. After few days, samples were air-dried and subjected to solubility measurements. For solubility measurements, duplicate 20-g samples of treated and untreated samples were placed into 250-mL Nalgene bottles with 100 mL of distilled–deionized H$_2$O. Three drops of toluene was added to each bottle to suppress microbial activity. Each sample bottle was tightly capped, placed on a mechanical shaker, and reacted in an incubator at a constant temperature of 25 °C (298 K). After 3- and 7-day reaction periods, sample suspensions were filtered through 0.45-μm Millipore filters under an atmosphere of argon gas to prevent uptake of atmospheric CO$_2$.

Each filtered solution was divided into two subsamples. One subsample was acidified to pH 5–6 with HNO$_3$. The other subsample was left unacidified. The unacidified samples were analyzed immediately for pH and concentration of carbonate species. The acidified samples were analyzed for Ca, Mg, Na, K, F, Mo, Cl, SO$_4$, and Si.

The pH was measured with an Orion combination pH electrode. Ca, Si, Mg, and Mo were measured with inductively coupled plasma optical emission spectroscopy
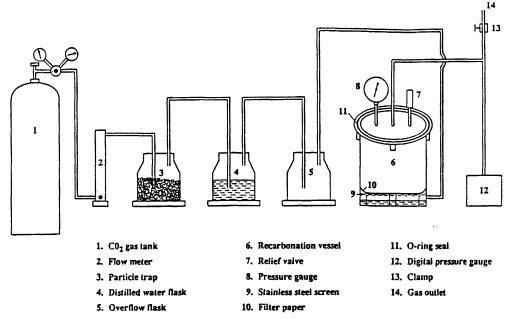
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1. CO_2 gas tank   6. Recarbonation vessel   11. O-ring seal
2. Flow meter   7. Relief valve   12. Digital pressure gauge
3. Particle trap   8. Pressure gauge   13. Clamp
4. Distilled water flask   9. Stainless steel screen   14. Gas outlet
5. Overflow flask   10. Filter paper

Figure 1. Experimental design of CO_2 pressure process to hasten recarbonation process of oil shale solid wastes

Table I. Effect of CO_2 Treatment on pH and Concentrations of Different Elements in Aqueous Extracts of Oil Shales[a]

	raw oil shale	PP3		Lurgi		PP6	
		BR[b]	AR[c]	BR[b]	AR[c]	BR[b]	AR[c]
				3 Days			
pH	7.93	10.28	9.00	11.62	9.05	11.65	9.07
Ca	108.0	0.22	11.04	156.0	18.32	205.0	252.0
Mg	44.0	0.24	12.18	BD[d]	313.0	BD[d]	266.0
Si	10.0	1.0	0.45	8.5	1.7	10.0	1.1
C[e]	176.0	351.0	157.0	1.4	68.0	4.2	5.3
F	3.5	15.1	9.5	8.5	1.9	2.13	6.74
Mo	0.43	1.6	1.45	1.1	0.83	4.80	1.10
				7 Days			
pH	8.21	10.68	8.83	12.07	9.10	12.10	9.13
Ca	139.0	7.63	6.96	179.0	14.0	50.50	201.0
Mg	53.1	0.24	10.13	0.22	286.0	0.21	232.0
Si	9.7	0.77	0.40	3.87	1.77	17.32	7.05
C[e]	113.6	367.0	202.0	2.02	76.8	3.51	21.10
F	8.10	25.63	10.68	5.12	1.9	3.79	6.74
Mo	0.60	1.70	1.35	0.90	0.95	2.58	·0.76

[a] Mean of duplicate analyses, units are milligrams per liter except for pH. [b] Before CO_2 treatment. [c] After CO_2 treatment. [d] BD, below detection limit of 0.001 mg/L. [e] Total carbonate and bicarbonate species measured as CO_2.

(ICP-OES); Na and K were measured with atomic absorption (AA) spectrometry. F and Cl were measured with specific ion electrodes, and SO_4 was measured by $BaCl_2$ precipitation. Carbonate and bicarbonate species in the aqueous extracts were analyzed by the CO_2 gas release method (11) to avoid possible interference from inorganic and organic anions. In this method, solutions were acidified to pH 4.5 and evolved $CO_2(g)$ was trapped in a basic solution under an atmosphere of argon. Aqueous extracts of OSSW were also analyzed for B, As, and Se, but the concentrations of these elements were found to be less than 0.01 mg L^{-1}. The Ca^{2+} activity in aqueous extracts was analyzed with a specific ion electrode to test for possible effects of organic complexation on Ca^{2+} activity (11).

The total elemental concentrations and pH of aqueous extracts were used as input to the GEOCHEM (12) speciation model to calculate ion activities. Solution species (e.g., $HSiO_4^{3-}$, SiO_4^{4-}, $CaH_3SiO_4^{+}$, $NaMoO_4^{0}$, $CaMoO_4^{0}$) that may be significant in alkaline solid waste solutions were added to the GEOCHEM database (13). From ion activities, ion activity products (IAPs) were calculated and compared

with solubility products (K_{sp}s) to evaluate the solid phases controlling the solubilities of Ca, Mg, F, and Mo before and after CO_2 treatment. We assumed that IAPs within ±0.50 log unit of K_{sp}s of solid phases represented equilibrium, and that the solid phase was a probable control on the concentrations of the ions involved.

Results and Discussion

The effect of CO_2 treatment on the pH and the solubilities of major and trace elements in aqueous extracts of oil shales is presented in Table I. The complete results of the chemical analyses are reported in Reddy et al. (14), and only data from the 7-day reaction period will be discussed here. The chemical analyses of aqueous extracts of raw oil shale are also included in Table I for comparison.

The processing of raw shale at different temperatures caused significant differences in the chemical composition of the aqueous extracts both before and after CO_2 treatment. The CO_2 treatment had least effect on the PP3 sample, presumably because it was processed at a temperature low enough for carbonates to be preserved.

Table II. Saturation Indexes Indicating Potential Controls on the Solubilities of Ca, Mg, F, and Mo in Aqueous Extracts of Oil Shales[a]

| | | saturation index[b] | | | | | |
| | | PP3 | | Lurgi | | PP6 | |
solid phase	log K_{sp}[c]	BR[d]	AR[e]	BR[d]	AR[e]	BR[d]	AR[e]
CaSiO$_3$ (wollastonite)	13.27			0.03	-3.34	-0.33	-2.52
CaCO$_3$ (calcite)	-8.48	-0.32	0.33		0.28		0.08
Mg$_2$SiO$_4$ (forsterite)	28.87					-0.17	-1.92
MgSiO$_3$ (clinoenstatite)	11.42				0.01		-0.25
Mg$_3$Si$_4$O$_{10}$(OH)$_2$ (talc)	22.26	0.44	0.17	0.14			
MgCO$_3$ (magnesite)	-7.46		-0.29		0.85		-0.44
CaF$_2$ (fluorite)	10.42	-0.09	-0.42	0.41	-1.84	-0.39	0.23
CaMoO$_4$ (powellite)	-8.05	-2.13	-1.60	-0.32	-2.30	-0.85	-1.17

[a] Mean of duplicate analyses. [b] log (IAP/K_{sp}). [c] Values were taken from Reddy et al. (13) and Reddy and Drever (20). Values for calcite and powellite were taken from Plummer and Busenburg (21) and Essington (5), respectively. [d] Before CO$_2$ treatment. [e] After CO$_2$ treatment.

Potential solubility controls on Ca, Mg, F, and Mo in aqueous extracts from treated and untreated samples are presented in Table II. A complete list of saturation indexes for different solid phases are reported in Reddy et al. (14), and only the few solid phases relevant to the comparison of before and after CO$_2$ treatment are discussed here. Before CO$_2$ treatment, IAPs for the PP3 sample extracts show a close approach to saturation with respect to calcite and talc. These results suggest that concentrations of Ca^{2+} and Mg^{2+} in PP3 aqueous extracts are probably controlled by calcite and a magnesium silicate phase such as talc. The IAPs for Lurgi and PP6 samples show a close approach to saturation with respect to wollastonite. The IAPs also show a close approach to saturation with respect to forsterite (for PP6) and talc (for Lurgi). These results suggest that silicate phases formed during high-temperature processing are controlling the concentrations of Ca^{2+} and Mg^{2+} in aqueous extracts from untreated Lurgi and PP6 samples.

Park et al. (15), Reddy and Lindsay (22), and Reddy et al. (13) have reported that processing raw shale at elevated temperatures causes production of oxides (e.g., CaO, MgO) and several silicate phases including wollastonite and forsterite. The oxide phases are more soluble than silicate phases and often dissolve upon contact with moisture. The IAPs of oxide phases for untreated Lurgi and PP6 samples also indicated a high degree of undersaturation. Thus, silicate phases produced during the process of heating usually buffer the pH and control Ca^{2+} and Mg^{2+} concentrations. However, for the PP3 sample, which was produced by processing raw shale at moderate temperatures (to minimize decomposition of carbonates), calcite is probably buffering the pH and controlling the concentration of Ca^{2+} in aqueous extracts.

The CO$_2$ treatment effectively lowered the pH of OSSW aqueous extracts from 12.0 to ~9.0 (Table I). The IAPs for the PP3 samples show a close approach to saturation with respect to calcite. The IAPs for Lurgi and PP6 samples show a high degree of undersaturation with respect to wollastonite and a close approach to saturation with respect to calcite. These results suggest that CO$_2$ treatment caused dissolution of wollastonite (and probably other silicate phases), precipitation of calcite, and reduction of pH.

Several other studies have also reported a decrease in pH of OSSW aqueous extracts due to recarbonation. Bell and Berg (16) reported that exposing OSSW to the atmosphere over a period of 20–160 days lowered the pH of extracts from 11.4 to 9.0 by recarbonation. Harbert et al. (17) attributed the decrease in pH of OSSW aqueous extracts to the precipitation of calcite. Reddy et al. (3) reported that bubbling CO$_2$ through aqueous extracts of

OSSW for 6 months caused dissolution of silicate phases, precipitation of calcite, and reduction of pH from 12.0 to ~8.0. In our experiments, reacting moist OSSW under slightly elevated CO$_2$ pressures for 1 h accelerated the recarbonation process and lowered the pH through the precipitation of calcite.

The Mg^{2+} concentrations in aqueous extracts of OSSW after CO$_2$ treatment appeared to be controlled by either the silicate or carbonate phase, the IAPs show a close approach to saturation with respect to talc, clinoenstatite, and magnesite.

The CO$_2$ treatment caused a decrease in the concentration of F for PP3 and Lurgi extracts, but not for PP6. The CO$_2$ treatment also caused a decrease in the concentrations of Mo for PP3 and PP6 samples. Reddy et al. (3) reported that lowering the pH of OSSW causes reduction in the concentrations of F and, in some cases, Mo in extracts. Garland et al. (7) and Essington and Spackman (23) have reported similar results. Thus, the decrease in the concentrations of F and Mo in CO$_2$-treated samples is probably due to the reduction in the pH of extracts. The IAPs both before and after CO$_2$ treatment show a close approach to saturation with respect to fluorite (except Lurgi after treatment) and a high degree of undersaturation with respect to powellite (except Lurgi before treatment). These results suggest that fluorite may be controlling the solubility of F, and that powellite does not control the solubility of Mo in aqueous extracts from either treated or untreated samples.

Stollenwerk and Runnells (2), Reddy and Hasfurther (6), Essington et al. (18), and Essington and Spackman (19) have reported that fluorite and powellite probably control the solubilities of F and Mo in aqueous extracts of OSSW, respectively. However, our study and that of Essington (5) suggest powellite does not always control the solubility of Mo in OSSW extracts.

Conclusions

The processing of oil shale at high temperatures results in production of large quantities of oil shale solid wastes. These waste materials are often alkaline and often contain elevated levels of toxic elements. Before CO$_2$ treatment, the solubility measurements suggested that silicate phases including wollastonite and forsterite (produced during the heating process) buffer the pH and control Ca^{2+} and Mg^{2+} concentrations in aqueous extracts of OSSW. Reacting moist OSSW at 5 psi CO$_2$ pressure for 1 h lowered the pH from 12.0 to 9.0 through the precipitation of calcite and also decreased the concentrations of F and Mo in aqueous extracts. The Ca^{2+} concentrations in CO$_2$-treated samples were controlled by the solubility of calcite. The Mg^{2+} concentration appeared to be controlled by silicate and

carbonate phases. The F^- concentrations from treated and untreated samples suggested a close approach to saturation with respect to fluorite. The MoO_4^{2-} concentrations appeared to be highly undersaturated with respect to powellite.

The CO_2 pressure process described in this study involves treatment of waste materials in a solid phase containing moisture, not a slurry or an aqueous solution phase, and requires only short reaction times (e.g., 1 h) to effectively lower the pH and the solubilities of F and Mo. Since this process uses CO_2, which can be obtained either from the combustion process itself or from other sources, another potential benefit is that it may help to minimize emission of CO_2 into the atmosphere. Further detailed research to examine the efficiency of the CO_2 pressure process for chemical stabilization of alkaline solid wastes (e.g., coal combustion solid waste) is needed.

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