

APPLICATION OF A GEOCHEMICAL MODEL TO THE
PREDICTION OF THE CHEMISTRY OF EXTRACTS FROM
NON-RECARBONATED AND RECARBONATED SPENT SHALES

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SUMMARY

The chemistry of extracts from spent shale disposal environments is controlled by a number of chemical processes including the formation of inorganic complexes and precipitation-dissolution reactions. Several geochemical codes such as EQ3/EQ6, GEOCHEM, MINTEQ, PHREEQE, and SOLMNEQ are available to predict these chemical processes. However, these codes lack data for solution species (association constants) and solid phases (solubility products) that are relevant to spent shale. The objectives of this study were (1) to alter the data base of a geochemical code by including data for different solution species and solid phases that are important to spent shale environments and (2) to predict the chemistry of extracts from non-recarbonated and recarbonated spent shales by evaluating the solid phases controlling the solubilities of major elements such as calcium and magnesium, and trace elements like fluorine and molybdenum.

The geochemical code used for this study was the GEOCHEM model. The data base of this code was altered using updated association constants and solubility products for different elements that we, and others have developed.

Three spent shale samples (PPP3, PPP6, and Lurgi) were recarbonated under slightly elevated CO₂ pressure in a specially designed chamber. The non-recarbonated and recarbonated samples were subjected to solubility studies. The total elemental concentrations and pH of extracts were used as input to the GEOCHEM code to predict the chemistry. The model predicted that silicate phases (produced during the heating process) initially buffered the pH and controlled Ca²⁺ and Mg²⁺ concentrations in extracts. The recarbonation process in spent shales probably dissolves silicates, precipitates carbonates, and reduces the pH of extracts to approximately 9.0. The GEOCHEM model predicted that after recarbonation, the Ca²⁺ concentrations are controlled by calcite. The Mg²⁺ concentrations may be controlled by both clinoenstatite and magnesite. The F⁻ concentrations in extracts from non-recarbonated and recarbonated spent shales are controlled by fluorite. Further, GEOCHEM predicted that powellite does not control the solubility of molybdenum in non-recarbonated recarbonated spent shale extracts.

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 waste (spent shale). During the processing of oil shale, high temperatures decompose carbonate minerals, and the pH of spent shale extracts approaches 12.0. This modifies the solubility relationships of major and trace elements. The mineral reactions that control Ca^{2+} and Mg^{2+} solubilities are important because they can explain the high alkalinity associated with spent shale extracts.

Parker et al. (1977) reported the chemical characteristics of groundwater from an in situ oil shale burn near Rock Springs, Wyoming. The F concentrations increased from 26.5 in the spent shales to 35.0 mgL^{-1} in the extracts. Similarly, the concentrations of B increased (from 8.5 to 40.0 mgL^{-1}) in groundwater. Stollenwerk and Runnells (1981) leached different spent shales over 140 days and report that high concentrations of B, F, and Mo released from spent shales may contaminate surface and groundwater resources. Garland et al. (1979), Harbert et al. (1979), Wildung and Zachara (1980), and Fransway and Wagenet (1981) report that soluble toxic elements may leach from a spent shale disposal environment and migrate to groundwater. Stark and Redente (1986) examined salt and trace element movement in spent shale disposal environments. These authors report a considerable downward movement of Na salts, F, and, to some extent, Mo from spent shale disposal environments. Other elements such as B, As, and Se show little or no movement out of disposal sites.

The behavior of different elements in spent shale disposal environments is controlled by a number of chemical processes including the formation of soluble inorganic complexes and precipitation-dissolution reactions. Several geochemical codes are available to examine these chemical processes. Reddy and Drever (1987) and Reddy et al. (1988) evaluated the application of geochemical codes such as EQ3/EQ6 (Worley 1979), GEOCHEM (Sposito and Mattigod 1980), MINTEQ (Felmy et al. 1984), PHREEQE (Parkhurst et al. 1980), SOLMNEQ (Kharaka and Barnes 1973), and WATEQFC (Runnells and Lindberg 1981) to predict chemistry of extracts from spent shales. Reddy and Drever (1987) and Reddy et al. (1988) report that these geochemical codes lack the data for accurate solution species and solid phases that are relevant to spent shale disposal environments. They also compiled thermodynamic data for these missing relevant solution species and solid phases.

When spent shales are exposed in a disposal environment, these materials absorb CO_2 from the atmosphere (recarbonation process). This reduces the pH of spent shale extracts to around 8.50. Thus, it is important to predict the chemistry of extracts from both non-recarbonated and recarbonated spent shales. Such information will be useful in developing effective reclamation methods to minimize pollution problems associated with the disposal of spent shales.

The objectives of this study were to alter the data base of a geochemical code by including data for different solution species and

solid phases that are important for spent shale environments and to predict the chemistry of extracts from unrecarbonated and recarbonated spent shales by examining the solid phases controlling the solubilities of major (e.g., Ca and Mg) and trace (e.g., F and Mo) elements.

METHODS

We evaluated EQ3/EQ6, GEOCHEM, MINTEQ, PHREEQE, SOLMNEQ, and WATEQFC geochemical codes and selected GEOCHEM to alter the database. The GEOCHEM model code was selected because it computes the highest number of elements (44), solution species (2000), and solid phases (500); and the database is rather simple to alter compared with other codes. The updated association constants and solubility constants for different solution species and solid phases that we expected to be significant in spent shale environments were included in the GEOCHEM database. For example, we included association constants for HSiO_4^{3-} , SiO_4^{4-} , HMoO_4^- , CaMoO_4^0 , NaMoO_4^- , KMoO_4^- , CaF^+ , MgF^+ , NaF^0 , KF^0 , CaSO_4^0 , MgSO_4^0 , NaSO_4^- , and KSO_4^- and solubility constants for wollastonite (CaSiO_3), diopside ($\text{CaMg}(\text{SiO}_3)_2$), monticellite (CaMgSiO_4), åkermanite ($\text{Ca}_2\text{MgSi}_2\text{O}_7$), merwinite ($\text{Ca}_3\text{MgSi}_2\text{O}_8$), calcite (CaCO_3), powellite (CaMoO_4), and fluorite (CaF_2). A complete list of solution species and solid phases for different elements is reported in Reddy and Drever (1987) and Reddy et al. (1988).

The samples used in this study to predict the chemistry from non-recarbonated and recarbonated spent shales were PPP3, PPP6, and Lurgi spent shales. Western reference Green River Formation oil shale from Piceance Creek Basin in Colorado was processed under conditions typical of the Paraho Process to produce PPP3 and PPP6 spent shales. The processing conditions used to produce these spent shales are summarized by Merriam et al. (1987). In addition to these spent shales, A Lurgi-processed oil shale was also used in this study. Processing conditions for the Lurgi process are reported by Nowacki (1981).

The spent shale samples were ground to pass a 0.25-mm sieve and used for solubility measurements and recarbonation studies. Duplicate, 20-g samples were placed into 250-mL Nalgene bottles with 100-mL of distilled-deionized H_2O . 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 constant 25°C (78°F). After 3 and 7 days reaction time, the sample suspensions were filtered through 0.45µm Millipore filters under an atmosphere of argon gas to minimize uptake of atmospheric CO_2 by spent shale extracts. Alkaline solutions can absorb atmospheric CO_2 , which will be converted to carbonates and bicarbonates to form solution species, if they are not placed in an inert gas environment. Once alkaline solutions absorb CO_2 , their true solution chemistry changed, and analysis of such solutions will lead to erroneous predictions of their chemistry.

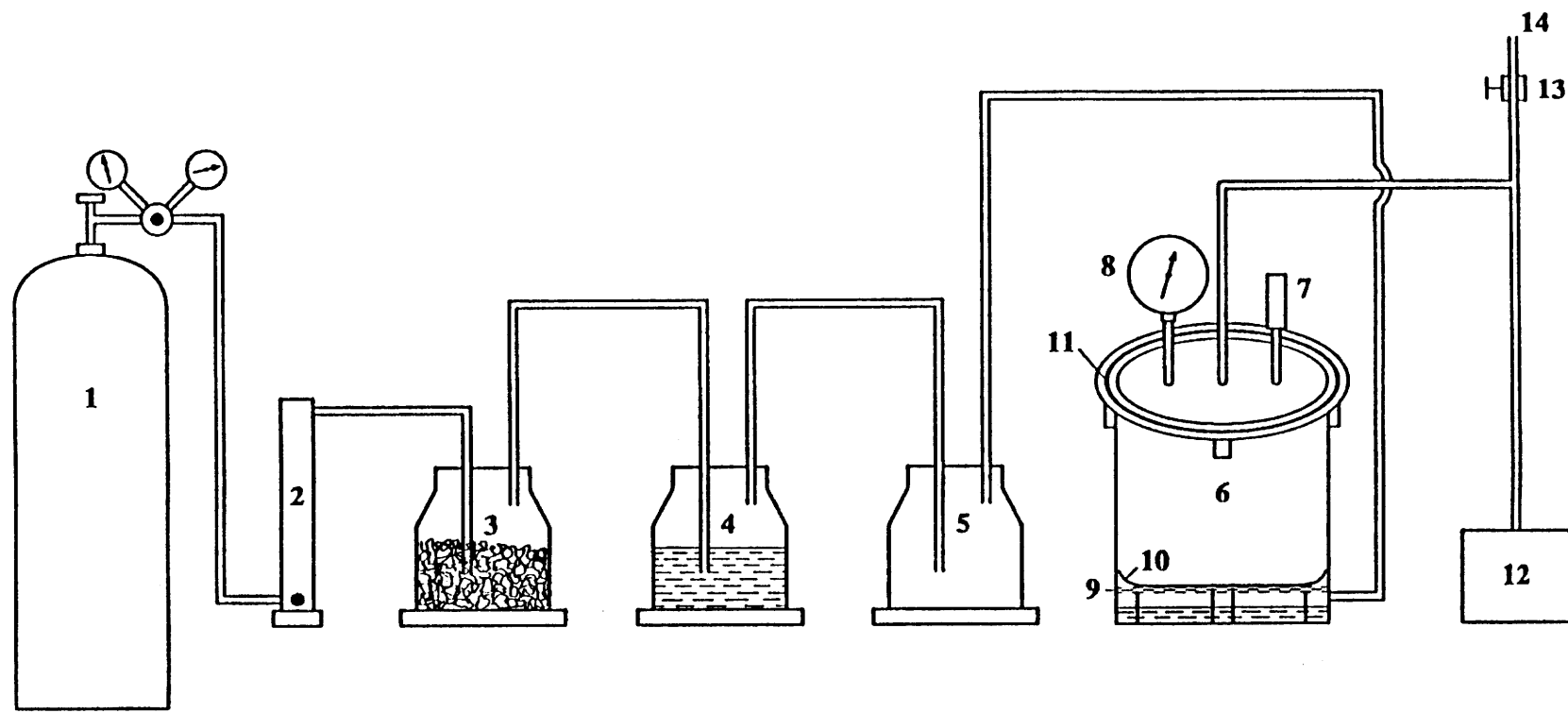
Each filtered extract was divided into two subsamples. One subsample was acidified with HNO_3 to a pH between 5 and 6. The other subsample was not acidified. The unacidified samples were analyzed

immediately for pH and concentration of carbonate species. The acidified samples were analyzed by Ca, Mg, Na, K, F, Mo, Cl, SO₄, and Si. The complete details of chemical analyses are discussed later in this section.

A recarbonation vessel was designed to lower the alkalinity of spent shales (Figure 1). The reaction vessel consisted of a 30-cm-diameter by 30-cm-long PVC cylinder with an o-ring seal lid. A pressure release valve was inserted on top of the lid to control the pressure inside the reaction vessel. A stainless steel screen with filter paper was placed in the middle of the reaction vessel to hold the sample. The gas outlet from the reaction vessel was connected to a digital pressure gauge to monitor pressure inside the reaction vessel. The gas inlet from the reaction vessel was connected to a digital pressure gauge to monitor pressure inside the reaction vessel. The gas inlet from the reaction vessel was connected to a distilled H₂O flask. The distilled H₂O flask was connected to a particle trap flask. Fifty grams of air-dried sample was spread over the filter paper. Before connecting the gas outlet to the digital pressure gauge, CO₂ gas from a gas tank was bubbled through distilled H₂O, using a sparger, to purge the initial air from the reaction vessel. Approximately 5 psig pressure was maintained inside the reaction vessel. After reacting for one hour, the sample was removed and sufficient distilled H₂O was added to the sample to prepare a saturated paste. The saturated paste was then subjected to wet and dry cycles under laboratory conditions. After several weeks, the samples were air dried and subjected to solubility measurements as explained earlier. This was repeated for each set of samples.

The chemical analyses of non-recarbonated and recarbonated spent shale extracts were performed using standard methods. The pH was measured with an Orion combination pH electrode. The electrode was buffered with pH 8.0 and 12.0 buffer solutions before pH measurements were taken. The Ca, Mg, Si, and Mo concentrations were measured using inductively coupled plasma optical emission spectroscopy (ICP-OES). The Na and K concentrations were measured using atomic absorption (AA).

The F and Cl concentrations were measured using Orion specific ion electrodes. In this method, electrodes were calibrated against known concentrations of F and Cl standard solutions provided by the Orion Company. The F and Cl concentrations in spent shale extracts were obtained by comparing the electrode values against standard values. The SO₄ concentrations were measured by the BaCl₂ precipitation method. The carbonate and bicarbonate concentrations were measured with the CO₂ gas release method (Reddy et al. 1990) to avoid interference by inorganic and organic anions. In this method, extracts were acidified to pH 4.50, and evolved CO₂ was trapped in a basic solution under an atmosphere of argon. The Ca²⁺ activity in extracts was also measured with an Orion specific ion electrode. This minimizes the possibility of overestimating Ca²⁺ activity due to organic complexes, because spent shale extracts may contain dissolved organic compounds (McKay and Lane 1988). In this method, the Ca²⁺ electrode was calibrated against CaCl₂ standards of known Ca²⁺ activity provided by Orion. The Ca²⁺ activity in extracts was obtained by comparing electrode values against standard Ca²⁺ activity values.



- | | | |
|-----------------------------|---------------------------|----------------------------|
| 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 for Recarbonation of Spent Shales

The total elemental concentrations and pH of non-recarbonated and recarbonated spent shale extracts were used as input to the GEOCHEM code to calculate ion activities. From ion activities, ion activity products (IAP) were calculated and compared with solubility products (K_{sp}) to predict the solid phases controlling the solubility of major and trace elements in spent shale extracts. We assumed that an IAP within ± 0.50 log units of the solid phase K_{sp} represents equilibrium and that the solid phase was a probable control on the concentrations of the ions involved. Greater than (supersaturation) or less than (undersaturation) ± 0.50 log units is a non-equilibrium state. The difference between IAP and K_{sp} values within that range is accounted for by the uncertainty of IAP measurements and K_{sp} values reported in the chemical literature.

RESULTS AND DISCUSSIONS

The chemical analyses of spent shale extracts are summarized in Table 1. The chemical analyses of raw shale extracts are also included in Table 1 for comparison. Only data from the 7-day reaction period will be discussed because these are the most uniform results.

The PPP3, PPP6, and Lurgi spent shales were produced by processing raw shale at 770, 1295, and 1000 K, respectively. These different processing temperatures generally increased pH, F, and Mo and decreased Ca, Mg, Si, and C concentrations in spent shale extracts. Recarbonation did not change the concentration of Ca in the PPP3 extracts. For the PPP6 and Lurgi, recarbonation caused an increase and a decrease in the concentration of Ca in extracts, respectively. Furthermore, recarbonation increased the concentration of Mg and decreased the concentration of Si in the spent shale extracts.

The saturation indices for the 7-day reaction period are summarized in Table 2. The results discussed in this section are based on the predictions made by the GEOCHEM code after altering the data base. Before recarbonation of the PPP3 sample, the IAPs show that calcite and talc are close to saturation. These results suggest that the Ca^{2+} and Mg^{2+} concentrations are probably controlled by calcite and talc, respectively. The IAPs for the PPP6 and Lurgi samples show that wollastonite is close to saturation. The IAPs also show saturation with respect to forsterite and talc. These results suggest that silicate phases are may be controlling the solubilities of Ca^{2+} and Mg^{2+} in spent shale extracts.

Park et al. (1979), Reddy and Lindsay (1986), Reddy et al. (1988), and several other researchers report that processing raw shale at high temperature produces oxide phases (e.g., CaO, MgO) and several silicate phases. The oxide phases are more soluble than silicate phases, and oxides commonly dissolve upon contact with moisture. Furthermore, IAPs of oxide phases in spent shale extracts suggest a high degree of undersaturation. Thus, silicate phases (produced during the heating process) initially buffer the pH and control Ca^{2+} and Mg^{2+} solubilities in spent shale extracts. However, because the PPP3 spent shale was produced by processing raw shale at a moderate temperature, not many carbonates decomposed (Reddy et al. 1988), and calcite continued to buffer pH and control the solubility of Ca^{2+} in extracts.

Table 1. Chemical Data of Raw and Spent Shale Extracts^a

Raw Shale	PPP3		PPP6		Lurgi		
	BR ^b	AR ^c	BR	AR	BR	AR	
	<u>3 days</u>						
pH	7.93	10.28	9.00	11.65	9.07	11.62	9.05
Ca	2.57	5.25	3.56	2.29	2.20	2.41	3.34
Mg	2.74	5.00	3.30	BD	1.96	BD	1.89
Na	2.52	1.20	1.40	1.56	1.61	3.04	2.43
K	3.55	3.12	3.25	2.17	2.59	3.36	2.81
Si	3.45	4.46	4.79	3.45	4.40	3.52	4.20
SO ₄	2.75	2.16	2.01	2.15	1.87	2.37	2.20
C ^d	2.54	2.24	2.59	4.16	4.06	4.63	2.95
Cl	2.30	1.63	2.00	1.82	1.52	3.50	3.30
F	3.74	3.10	3.30	3.95	3.45	3.35	4.00
Mo	5.35	4.78	4.82	4.30	4.94	4.94	5.06
	<u>7 days</u>						
pH	8.21	10.68	8.83	12.10	9.13	12.07	9.10
Ca	2.46	3.72	3.76	2.90	2.30	2.35	3.46
Mg	2.66	5.00	3.38	5.06	2.02	5.03	1.93
Na	2.47	0.89	1.38	1.14	1.69	2.48	2.36
K	3.50	3.09	3.23	2.18	2.64	2.98	2.86
Si	3.46	4.56	4.85	3.21	3.60	3.86	4.20
SO ₄	2.39	1.76	1.95	1.95	1.95	2.75	2.27
C ^d	2.73	2.22	2.48	4.24	3.46	4.48	2.90
Cl	3.77	1.30	2.00	1.70	1.60	3.30	2.00
F	3.70	2.87	3.25	3.70	3.45	3.57	4.00
Mo	5.20	4.75	4.83	4.57	5.10	5.03	5.00

^a Mean of duplicate analyses, -log mol/L

^b Before recarbonation

^c After recarbonation

^d Inorganic carbonate and bicarbonate species

BD = below the detection limit (0.001 mg/L)

Table 2. Solid Phases Controlling the Solubilities of Ca, Mg, F, and Mo in Spent Shale Extracts^a

Solid Phase	log K_{sp} ^c	Saturation Index ^b					
		PPP3		PPP6		Lurgi	
		BR ^d	AR ^e	BR	AR	BR	AR
CaO lime	33.00	-16.30	-19.24	-12.25	-17.48	-11.74	-18.76
Ca(OH) ₂ portlandite	23.02	-6.32	-9.26	-2.27	-7.50	-1.76	-8.78
CaSiO ₃ wollastonite	13.27	-2.46	-4.44	-0.33	-2.52	0.03	-3.34
CaSiO ₃ pseudo- wollastonite	14.23	-3.42	-5.40	-1.30	-3.32	-1.09	-4.50
Ca ₂ MgSi ₂ O ₇ åkermanite	46.10	-8.98	-14.39	-1.88	-8.50	-1.79	-10.90
CaMgSiO ₄ monticellite	30.32	-3.99	-7.44	0.97	-3.64	0.85	-4.85
Ca ₃ MgSi ₂ O ₈ merwinite	-13.69	25.11	23.56	30.26	30.41	31.26	26.95
Ca ₃ SiO ₇ rankinite	49.28	-10.98	-17.86	-2.67	-11.94	-1.74	-15.58
β-Ca ₂ SiO ₄ laranite	39.62	-12.11	-17.03	-5.94	-13.19	-5.22	-15.65
γ-Ca ₂ SiO ₄ calcium olivine	37.82	-10.31	-15.23	-4.14	-11.39	-3.42	-13.85
CaMg(SiO ₃) ₂ diopside	21.60	-1.18	-3.65	1.87	0.60	1.45	-0.64
MgO periclase	21.74	-6.22	-7.69	-3.38	-5.96	-3.71	-6.00
Mg(OH) ₂ brucite	16.84	-1.32	-2.79	1.52	-1.06	1.19	1.10
MgSiO ₃ clinoenstatite	11.42	-1.79	-2.30	-0.90	-0.25	-1.51	0.01

Table 2. Solid Phases Controlling the Solubilities of Ca, Mg, F, and Mo in Spent Shale Extracts^a (Continued)

Solid Phase	log K_{sp} ^c	Saturation Index ^b					
		PPP3		PPP6		Lurqi	
		BR ^d	AR ^e	BR	AR	BR	AR
Mg ₂ SiO ₄ forsterite	28.87	-3.72	-5.70	-0.17	-1.92	-0.93	-1.90
Mg ₃ Si ₂ O ₅ (OH) ₄ chrysotile	32.87	1.91	-0.60	6.57	5.25	4.98	5.33
Mg ₃ Si ₄ O ₁₀ (OH) ₂ talc	22.26	0.44	0.17	1.54	6.64	0.14	7.52
Mg _{2.825} Si ₂ O ₅ (OH) _{3.65} antigorite	30.32	-10.18	-10.44	-9.88	-4.25	-12.01	-3.95
Mg ₆ Si ₄ O ₁₀ (OH) ₈ serpentine	61.75	7.81	2.83	17.13	14.49	-12.01	11.82
Mg ₂ Si ₃ O ₆ (OH) ₄ sepiolite	15.89	2.52	-2.58	-2.63	1.84	-4.19	2.06
Mg ₇ Si ₈ O ₂₂ (OH) ₂ anthophyllite	69.78	-8.26	-9.87	-3.82	3.80	8.53	4.32
CaSO ₄ ·2H ₂ O gypsum	-4.64	-2.26	-1.81	-1.29	-0.70	-1.81	-1.86
CaCO ₃ calcite	-8.48	-0.32	-0.33	-	0.08	-	0.28
MgCO ₃ magnesite	-7.46	-1.03	-0.29	-3.13	-0.44	-3.66	0.85
CaMg(CO ₃) ₂ dolomite	-17.85	2.05	1.95	-0.94	1.15	-1.14	3.05
CaF ₂ fluorite	-10.41	-0.09	-0.42	-0.39	0.23	0.41	-1.84
CaMoO ₄ powellite	-8.05	-2.13	-1.60	-0.85	-1.17	-0.32	-2.30

^a Mean of duplicate analyses

^b log (IAP/ k_{sp})

^c Values were taken from Reddy et al. (1988) and Reddy and Drever (1987).
Values for calcite and powellite were taken from Plummer and Busenburg (1982) and Essington (1990), respectively.

^d Before recarbonation

^e After recarbonation

The pH of spent shale extracts decreased from 12.0 to around 9.0 after recarbonation (Table 1). The IAPs for the PPP3 show a close saturation with respect to calcite. The show that for the PPP6 and Lurgi samples are highly undersaturated with respect to wollastonite and very nearly saturated with respect to calcite (Table 2). Thus, GEOCHEM predicted that recarbonation will probably dissolve silicate phases, precipitate carbonate phases, and reduce the pH. Several other studies report a decrease in the pH of spent shale extracts due to recarbonation. Bell and Berg (1977) report that exposing spent shale to the atmosphere decreases the pH of extracts from 11.4 to 9.0 by recarbonation. Harbert et al. (1979) attribute a decrease in the pH of spent shale extracts to precipitation of calcite. Reddy et al. (1986) report that bubbling CO₂ through spent shale extracts dissolved silicate phases, precipitated a calcite phase, and reduced the pH from 12.0 to around 8.0. Stollenwerk and Runnells (1981) and Essington and Spackman (1986) also report a decrease in the pH of spent shale extracts due to recarbonation.

The Mg²⁺ concentration in spent shale extracts after recarbonation may be controlled by both silicate and carbonate phases; the IAPs show saturation with respect to talc, clinoenstatite, and magnesite (Table 2). These results suggest that recarbonation will probably precipitate both silicate and carbonate phases, and these phases probably can coexist and control the Mg²⁺ solubility in extracts.

Recarbonation decreased the concentration of F in the PPP3 and Lurgi extract. Recarbonation also decreased the concentrations of Mo in the PPP3 and PPP6 extracts (Table 1). Reddy et al. (1986) report that lowering the pH of spent shales reduces the concentrations of F and, in some cases, Mo in extracts. Garland et al. (1979) and Essington and Spackman (1988) also report similar results. Thus, the decrease of F and Mo concentrations in recarbonated spent shales is probably due to the lower of the extracts. The GEOCHEM code predicted that extracts from non-recarbonated and recarbonated samples will be saturated with respect to fluorite and undersaturated with respect to powellite (Table 2). These results suggest that fluorite controls the solubility of F and that powellite does not control the solubility of Mo in spent shale extracts.

Stollenwerk and Runnells (1981), Reddy and Hasfurther (1989), Essington et al. (1987), and Essington and Spackman (1986) report that fluorite and powellite probably control the solubilities of F and Mo respectively, in spent shale extracts. However, our study suggests that powellite does not control the solubility of Mo in spent shale extracts from non-recarbonated and recarbonated samples. Another more stable Mo solid phase may be controlling the solubility of Mo in these extracts. Recently, Essington (1990) reports similar results and demonstrates the significance of CaMoO₄⁰, KMoO₄⁻, and NaMoO₄⁻ species in predicting the solid phase that controls the solubility of Mo in spent shale extracts.

CONCLUSIONS

The GEOCHEM database was altered with updated ion association constants and solubility constants for different solution species and solid phases, respectively, that are relevant to spent shale disposal environments. The GEOCHEM code was used to predict the chemistry of extracts from non-recarbonated and recarbonated spent shales. The results suggest that silicate phases, including wollastonite and forsterite (produced during the heating process), buffer the pH and control Ca^{2+} and Mg^{2+} concentrations in spent shale extracts. The Ca^{2+} concentrations in recarbonated samples were controlled the calcite, whereas the Mg^{2+} concentrations were controlled by silicate and carbonate phases. The F concentrations in extracts from non-recarbonated and recarbonated samples suggest that fluorite is close to saturation. The MoO_4^{2-} concentrations are highly undersaturated with respect to powellite. In general, recarbonation decreased the pH from 12.0 to 9.0, which resulted in the decrease of F and Mo concentrations in spent shale extracts.

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DISCLAIMER

Mention of specific brand names or models of equipment is for information only and does not imply endorsement.

NOTICE

The results and findings of this study are subject to different interpretations and are not necessarily supported by WRI.

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