

**GEOCHEMICAL MODELING TO PREDICT
THE CHEMISTRY OF LEACHATES FROM
ALKALINE SOLID WASTES: OIL SHALE
DEPOSITS, WESTERN U.S.A.**

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Geochemical modeling to predict the chemistry of leachates from alkaline solid wastes: oil shale deposits, western U.S.A.

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Abstract—Oil shale processing at elevated temperatures to extract oil results in large amounts of alkaline oil shale solid wastes (OSSW). The objective of this study was to use a geochemical model to help predict the chemistry of leachates, including toxic chemicals, from OSSW. Several geochemical models were evaluated (e.g. EQ3/EQ6, GEOCHEM, MINTEQA2, PHREEQE, SOLMINEQ, WATEQFC); the model GEOCHEM was selected based on its more comprehensive capabilities. The OSSW samples were subjected to solubility and XRD studies. Element concentrations and pH of OSSW leachates were used as input to GEOCHEM to predict their chemistry. Ion activity products were used to infer the likely solid phases controlling the concentration of toxic elements (e.g. F and Mo) in these leachates. The model predicted that silicate phases produced during the heating process buffered the pH and controlled concentrations of major cations. The F concentrations in OSSW leachates appeared to be controlled by fluorite (CaF₂). Contrary to previous findings, powellite (CaMoO₄) probably does not control the concentrations of Mo in OSSW leachates.

INTRODUCTION

OIL SHALE deposits in the western U.S.A. contain 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 OSSW are often alkaline (typical leachate pH may range from 10.0 to 13.0) and often contain elevated levels of toxic elements, particularly F and Mo (PARKER *et al.*, 1977; STOLLENWERK and RUNNELLS, 1981; STARK and REDENTE, 1986; ESSINGTON, 1990). One of the major environmental issues associated with the disposal of OSSW is prediction of the behavior of potentially toxic elements in the OSSW environments.

The behavior of various elements in OSSW environments is controlled by a number of chemical processes including the formation of soluble inorganic complexes and precipitation-dissolution reactions. Several geochemical models are available to predict the above chemical processes. However, each model differs in the environments to which it applies (NORDSTROM *et al.*, 1979). Thus, the objective of this study was to examine the applicability of existing geochemical models to predict the chemistry of leachates from OSSW.

MATERIALS AND METHODS

In order to evaluate the applicability of existing geochemical models for OSSW, the following criteria were established for preliminary screening of models:

1. Is the model in the public domain?
2. Is the model well documented?
3. Is the model in use and being kept updated?
4. Is the model able to model processes of interest, or could it be readily modified to include such processes?

Having met the above criteria, the following six models were obtained and examined in detail:

1. EQ3/EQ6 (WOLERY, 1979)
2. GEOCHEM (SPOSITO and MATTIGOD, 1980)
3. MINTEQA2 (FELMY *et al.*, 1984)
4. PHREEQE (PARKHURST *et al.*, 1980)
5. SOLMINEQ (KHARAKA *et al.*, 1988)
6. WATEQFC (RUNNELLS and LINDBERG, 1981).

To examine the applicability of the above models to OSSW, laboratory experiments were conducted to generate the solubility data. Samples used in this study were PPP3 (Paraho Pilot Process), Lurgi and PPP6. A reference sample of the Green River Formation oil shale from the Piceance Creek Basin in Colorado was used in this study. The reference sample was processed at 770, 1000 and 1295K to produce PPP3, Lurgi and PPP6 OSSW, respectively. Samples were ground to pass a 0.25 mm sieve and used for solubility and XRD studies. Duplicate, 20 g samples were placed into 250 ml Nalgene bottles with 100 ml of distilled-deionized H₂O. Three drops of toluene were added to each bottle to suppress microbial activity. Each sample bottle was tightly capped, placed on a mechanical shaker, and

Table 1. Capabilities of selected geochemical models

Capability	EQ3/EQ6	GEOCHEM	MINTEQA2	PHREEQE	SOLMINEQ	WATEQFC
Number of elements	18	44	32	35	30	34
Number of species	140	2000	373	296	340	500
Number of minerals	250	500	238	374	220	375
Speciation/saturation	Yes	Yes	Yes	Yes	Yes	Yes
Adsorption	No	Yes	Yes	No	Yes	No
Ion exchange	No	Yes	No	No	Yes	No
Organic complexation	No	Yes	No	No	Yes	No
Mass transfer	Yes	No	No	Yes	Yes	No
Temperature range, °C	0-300	25	0-300	—	0-350	0-100
Pressure range, bars	1-500	1	—	—	1-1000	1
Data base						
Easily modified	Yes	Yes	Yes	Yes	No	Yes

reacted in an incubator at a constant temperature of 25°C (298K).

After 3 and 7 d reaction time, the sample suspensions were filtered through 0.45 µm Millipore filters under an atmosphere of Ar gas to minimize uptake of atmospheric CO₂ by OSSW leachates. Each filtered extract was divided into two subsamples. One subsample was acidified to between a pH of 5 and 6 with HNO₃. 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, SO₄, and Si. The pH was measured with an Orion combination pH electrode. The Ca, Mg, Si, and Mo concentrations were measured with inductively coupled plasma optical emission spectroscopy (ICP-OES). The Na and K concentrations were measured with atomic absorption (AA). The F and Cl concentrations were measured using Orion specific ion electrodes. For each measurement, 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.*, 1990a) 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 Ar.

Element concentrations and pH of aqueous extracts were used as input to the selected geochemical model to calculate ion activities. From ion activities, ion activity products (IAPs) were calculated and compared with recently published solubility products (K_{sp} s for interpretation of the chemistry of OSSW. It was assumed that IAPs within ± 0.50 log units 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. The differences within that range is accounted for the uncertainty of IAP and K_{sp} measurements in the chemical literature (STUMM and MORGAN, 1981). The XRD analysis of samples was performed on randomly oriented samples with a Scintag PAD V powder diffractometer using Ni-filtered CuKα radiation.

RESULTS AND DISCUSSION

Table 1 summarizes the general features of the models, such as total number of elements, aqueous species and solid phases, and the temperature and pressure ranges over which calculations can be made. GEOCHEM, MINTEQA2, SOLMINEQ and

WATEQFC are speciation and saturation models; EQ3/EQ6 and PHREEQE are mass transfer as well as saturation models. Significant differences were found in the thermodynamic databases. All of the models lacked data for certain solid phases and solution species, which are expected to be significant in OSSW environments.

Based on the model evaluation, GEOCHEM was selected for inputting new or altered values into its database because it not only computes the highest number of elements (44), solution species (2000) and solid phases (500) but the thermodynamic database is the easiest to update. Updated association constants and solubility constants for different solution species and solid phases were (REDDY *et al.*, 1990b) included in the GEOCHEM database. For example, association constants for H₂SiO₄²⁻, HSiO₄³⁻, SiO₄⁴⁻, CaH₃SiO₄⁺, Ca(H₃SiO₄)₂⁰, MgH₃SiO₄⁺, Mg(H₃SiO₄)₂⁰, MoO₄⁰, HMoO₄⁻, CaMoO₄⁰, NaMoO₄⁻, KMoO₄⁻, CaF⁺, MgF⁺, NaF⁰, KF⁰, CaSO₄⁰, MgSO₄⁰, NaSO₄⁻, and KSO₄⁻ and solubility constants for wollastonite (CaSiO₃), diopside (CaMg(SiO₃)₂), monticellite (CaMgSiO₄), akermanite (Ca₂MgSi₂O₇), merwinite (Ca₃MgSi₂O₆), calcite (CaCO₃), powellite, (CaMoO₄), and fluorite (CaF₂) were included. The chemical analyses of raw and spent shale leachates are summarized in Table 2. The complete

Table 2. Chemical data of raw and OSSW leachates for a 7-d reaction period (-log mol/l; concentration mean of duplicates)

	Raw shale	PPP3	Lurgi	PPP6
pH	8.21	10.68	12.07	12.10
Ca	2.46	3.72	2.35	2.90
Mg	2.66	5.00	5.03	5.06
Na	2.47	0.89	2.48	1.14
K	3.50	3.09	2.98	2.18
Si	3.46	4.56	3.86	3.21
SO ₄	2.39	1.76	2.75	1.95
C*	2.73	2.22	4.48	4.24
Cl	3.77	1.30	3.30	1.70
F	3.70	2.87	3.57	3.70
Mo	5.20	4.75	5.03	4.57

*Inorganic carbonate and bicarbonate species.

Table 3. Potential solid phases controlling the solubilities of Ca, Mg, F and Mo in OSSW leachates (mean of duplicates)

Solid phase	Saturation Index (log IAP/ K_{sp})			
	log K_{sp}	PPP3	Lurgi	PPP6
Ca(OH) ₂ (portlandite)	23.02	-6.32	-1.76	-2.27
CaSiO ₃ (wollastonite)	13.27	-2.46	0.03	-0.33
Ca ₂ MgSi ₂ O ₇ (akermanite)	46.10	-8.98	-1.79	-1.88
CaMg(SiO ₃) ₂ (diopside)	21.60	-1.18	1.45	1.87
Mg(OH) ₂ (brucite)	16.84	-1.32	1.19	1.52
MgSiO ₃ (clinoenstatite)	11.42	-1.79	-1.51	-0.9
Mg ₂ SiO ₄ (forsterite)	28.87	-3.72	-0.93	-0.17
Mg ₃ Si ₄ O ₁₀ (OH) ₂ (talc)	22.26	0.44	0.14	1.54
CaSO ₄ ·2H ₂ O (gypsum)	-4.64	-2.26	-1.81	-1.29
CaMg(CO ₃) ₂ (dolomite)	-17.85	2.05	-1.14	-0.94
CaF ₂ (fluorite)	-10.41	-0.09	0.41	-0.39
CaMoO ₄ (powellite)	-8.05	-2.13	-0.32	-0.85

results of the chemical data are reported in REDDY *et al.* (1990b). The data from the 7 d reaction period only is used here because it provided the most uniform results.

Processing of raw shale at high temperatures caused a general increase in pH, F and Mo and a decrease in Ca, Mg, Si and C in OSSW leachates. Potential solubility controls on Ca, Mg, F and Mo in leachates from OSSW samples are presented in Table 3. A complete list of saturation indices for different minerals is reported in REDDY *et al.* (1990b), and only a few minerals relevant to the results are discussed here. For the PPP3 sample, the IAPs show that calcite and talc are close to saturation, suggesting that the Ca and Mg concentrations are probably controlled by calcite and talc, respectively. The IAPs for the PPP6 and Lurgi samples show that wollastonite, forsterite and talc are close to saturation, suggesting that silicate phases formed during high-temperature processing are probably controlling the solubilities of Ca and Mg in the leachates.

Major minerals identified by the XRD analysis are listed in Table 4. Processing raw shale at elevated temperatures causes decomposition of carbonate phases (e.g. calcite, dolomite) and production of oxide phases (e.g. periclase) and silicate phases (e.g. akermanite, diopside). Several other studies have reported similar results (PARK *et al.*, 1979; ESSINGTON *et al.* 1987; MASON *et al.*, 1984). Oxide phases are generally more soluble than silicate phases, and often dissolve upon contact with moisture. The IAPs of

oxide phases in spent shale leachates indicated a high degree of undersaturation. Thus, silicate phases produced during the process of heating appear to buffer the pH and control Ca and Mg solubilities in the leachates. However, carbonates in the PPP3 sample, which was produced by processing raw shale at a moderate temperature, did not decompose completely, and calcite was still buffering the pH and controlling the solubility of Ca in leachates.

Several studies (STOLLENWERK and RUNNELS, 1981; REDDY and HASFURTHER, 1989; ESSINGTON *et al.*, 1987) have reported that fluorite and powellite probably control the solubilities of F and Mo in OSSW leachates, respectively. However, the IAPs in this study show a close approach to saturation with respect to fluorite and a high degree of undersaturation with respect to powellite, except for the Lurgi sample. These results suggest that fluorite may be controlling the solubility of F, and that powellite does not control the solubility of Mo in OSSW leachates.

CONCLUSIONS

Evaluation of the geochemical models EQ3/EQ6, GEOCHEM, MINTEQA2, PHREEQE, SOLMINEQ and WATEQFC suggested that these models lack thermodynamic data for solid phases and solution species that are important for OSSW environments. GEOCHEM was selected and modified with updated thermodynamic data for different solution

Table 4. Major minerals identified in raw shale and OSSW samples (processing temperature, K, in parenthesis)

Raw shale	PPP3 (770)	Lurgi (1000)	PPP6 (1295)
Dolomite	Dolomite	Quartz	K-feldspar
Quartz	Quartz	Calcite	Quartz
Calcite	Calcite	Wollastonite	Calcite
Analcime	Akermanite	K-feldspar	Periclase
K-feldspar	K-feldspar	Periclase	Diopside

species and solid phases to predict the chemistry of leachates from OSSW. The model indicated that silicate phases including wollastonite and forsterite, produced during the heating process, probably buffer the pH and control Ca and Mg concentrations. Fluoride concentrations suggested a close approach to saturation with respect to fluorite. The Mo concentrations were highly undersaturated with respect to powellite.

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