**Laboratory Weathering and Solubility
Relationships of Fluorine and Molybdenum
in Combusted Oil Shale**

Topical Report

**M.E. Essington
R.A. Wills
M.A. Brown**

January 1991

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For
U.S. Department of Energy
Office of Fossil Energy
Morgantown Energy Technology Center
Morgantown, West Virginia

By
Western Research Institute
Laramie, Wyoming

MASTER

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SUMMARY

Proper management of large volumes of spent oil shale requires an understanding of the mineralogy and the disposal environment chemistry. Simulated laboratory weathering is one method to rapidly and inexpensively assess the long-term potential for spent oil shales to degrade the environment. The objectives of this study were to assess the solubility relationships of fluorine (F) and molybdenum (Mo) in Green River Formation spent oil shale, to examine the mineralogy and leachate chemistry of three combusted oil shales in a laboratory weathering environment using the humidity cell technique, and to examine the data from spent oil shale literature. Combusted oil shales from the Green River Formation and New Albany Shale were used in the examination of the leachate chemistry and mineralogy.

Combusted western oil shale mineralogy is dependent on the process conditions. In general, the process will result in the formation of anhydrite, lime, periclase, and hematite. During the initial stages of weathering, lime, periclase, and anhydrite dissolve and calcite precipitates. Also, ettringite precipitates during the initial weathering stages. In western disposal environments spent oil shale will remain in the initial stages of weathering, and highly alkaline and saline conditions will dominate the leachate chemistry. A leachate pH of 12.0 is rapidly reduced to between 8.5 and 9.0 with leaching.

The combusted eastern oil shale is composed of quartz, illite, hematite, and orthoclase. In an eastern disposal environment, soluble salts will be rapidly removed from the spent oil shale to potentially affect the surrounding environment. The combusted eastern oil shale did not display a potential to produce acid drainage. Leachate chemistry was dominated by Ca and SO_4 , and the element concentrations decreased with weathering.

Fluorine and Mo may adversely affect vegetation, grazing animals, groundwater, and surface waters that are proximate to spent oil shale disposal environments. The chemistry of F and Mo in spent oil shale leachates may be controlled by the precipitation of fluorite (CaF_2) and powellite (CaMoO_4), respectively. Thus, the fate and behavior of these elements may be predicted using equilibrium solubility methods.

Recent findings and the examination of methods cast doubt on the interpretations of many spent oil shale solubility studies. Recent research shows that the formation of soluble molybdate species in spent oil shale leachates can be significant. Further, reaction times necessary to achieve equilibrium conditions were not attained in many solubility experiments. Also, most of the solubility experiments were only performed on fresh solid waste, yielding little information on element behavior in a disposal environment. Examination of the literature data on ion association models suggests that F is present as CaF_2 in spent oil shale. However, spent oil shale leachates are undersaturated with respect to CaMoO_4 . During the initial cycles of the equilibrium weathering study, the solubility relationships for F and Mo were similar to those found in the literature. As weathering progressed, the spent oil shale leachates became supersaturated with

respect to fluorite and saturated with respect to powellite. These results indicate that in a weathering spent oil shale environment, subject to the slow infiltration of water, the behavior of Mo may be predicted on the basis of powellite solubility. However, F behavior can not be predicted due to the fact that the system becomes supersaturated over time as a result of an unknown factor. The leachate should not become supersaturated with F if CaF_2 is present and equilibrium exists.

INTRODUCTION

Spent oil shale is the solid waste product that results from the production of synthetic crude oil during the thermal alteration of oil shale. A commercial-scale shale oil operation will generate large quantities of solid waste materials. The Unocal operation at Parachute, Colorado, produced 95,400 m³ of synthetic crude oil and 675,000 t of spent oil shale in 1987 from a shale ore averaging 55% of design capacity (Knutson et al. 1988). Routson et al. (1979) estimated that the production of spent oil shale from a mature shale oil industry would exceed 1×10^{12} grams per day.

Spent oil shale mineralogy is a function of the raw oil shale properties (e.g., mineralogy, grain size, organic matter content) and the process parameters (e.g., heating rate, maximum temperature and duration, gas composition, porosity) (Campbell and Burnham 1978; Park et al. 1979; Williamson et al. 1980). The mineralogy of the raw oil shale and the oil shale processing parameters are factors that directly influence spent oil shale leachate chemistry. In general, the heat-induced mineral alterations that occur during the processing of oil shale result in a suite of minerals, principally alkaline earth oxides and silicates, that generate highly alkaline and saline leachates. Batch extraction and laboratory column studies are commonly employed to rapidly assess the potential for spent oil shale to generate leachates that contain elevated levels of potentially hazardous elements, salinity, sodicity, and alkalinity (or acidity) (Fransway and Wagenet 1981; Grant et al. 1981; Koppenaal et al. 1981; Stollenwerk and Runnells 1981; Saffer et al. 1982; Tian and Ehmann 1984; Jones 1990). Although batch extraction tests provide valuable information, there are a number of inherent limitations with respect to the applicability of the results (Jones 1990). The tests do not allow for the assessment of leachate and mineralogical character as a function of exposure in a weathering environment, and the data obtained are only applicable to the waste at that particular stage of weathering.

Batch extraction tests that impose artificial conditions to simulate the long-term release of elements (e.g., TCLP extraction, acid leaching, chelate leaching) may produce ambiguous results (Esmaili et al. 1985; Essington and Carroll 1985; Jones 1990). Such artificial conditions do not allow for the natural progression of weathering, denoted by the dissolution of unstable minerals, the migration of soluble salts, and the precipitation of stable minerals. Such reactions are significant with respect to spent oil shale, due to their inherent instability, and may result in the fixation or the slow release of elements (Essington 1989a).

Leachates from field lysimeters or actual spent oil shale disposal sites, as well as the weathered solids, have also been examined (Garland et al. 1979; Richardson et al. 1981; Tuttle et al. 1985; Robl et al. 1985, 1986, 1987; Stark and Redente 1986, 1990a, b). Field studies provide the most relevant information on solid waste behavior in a disposal environment. However, such studies are time consuming and costly, and it may take decades before spent oil shale leachates affect the surrounding environment. For example, Tuttle et al. (1985)

determined the mineralogy and elemental abundances for a 50-year-old retorted oil shale waste disposal pile at an experimental retort facility in Rulison, Colorado. They reported that limited changes had occurred over the past 50 years, as weathering products were only observed at shallow depths in the disposal pile.

The alkalinity, salinity, and potentially hazardous element composition of a spent oil shale leachate are influenced by the mineralogy of the solid waste material. Further, the leachability of these components is a function of the hydrology of the disposal pile (e.g., annual precipitation). Thus, methods that adequately assess the long-term potential for the solid waste material to adversely affect the environment must include a mechanism to examine waste behavior on a waste-specific and site-specific basis. Relatively short-term, cost-effective procedures for such an evaluation include the Soxhlet and the humidity cell weathering procedures (Caruccio 1968; Sobek et al. 1982). These methods are relatively short-term and can generate trends in mineralogical alterations and trends in leachate behavior (as a function of time) that may occur in a field environment under a variety of conditions. Oil shale, spent oil shale, and coal refuse and overburden have been subjected to laboratory weathering using these and similar methods, primarily to assess acid drainage potential (Koppelaar et al. 1981; Sullivan and Sobek 1982; Sullivan et al. 1986, 1987a, b). One of the objectives of the present study is to use the humidity cell laboratory weathering technique to examine combusted western (Green River Formation) and eastern (New Albany Shale) oil shale mineralogy and leachate chemistry as a function of relative time in a nonequilibrium, unsaturated leaching environment.

Potentially toxic levels of molybdenum (Mo) and fluorine (F) leached from spent oil shale disposal environments may adversely affect vegetation, grazing animals, groundwater, and surface waters. Molybdenum is an essential plant micronutrient; it can be accumulated in plant tissue without phytotoxic effects to levels that are toxic to grazing animals. Plant uptake of Mo from soils is directly correlated to Mo concentrations in soil solutions (Adriano 1986; Albasel and Pratt 1989). Correspondingly, plants grown on spent oil shale may accumulate Mo as a result of elevated Mo concentrations in spent oil shale solutions. Indeed, the concentrations of Mo and Cu/Mo ratios in plants grown on spent oil shale suggest that molybdenosis can be expected in grazing animals (Kilkelly and Lindsay 1982; Schwab et al. 1983; Reddy and Lindsay 1987; Stark and Redente 1990a, b).

Fluorine has not been shown to be an essential plant nutrient but may be concentrated in plant tissue without phytotoxic effects to levels that can cause fluorosis in grazing animals (Adriano 1986). Plants grown on spent oil shale, recarbonated spent oil shale, and topsoil (<30 cm) over spent oil shale may accumulate F (Kilkelly and Lindsay 1982; Schwab et al. 1983; Reddy and Lindsay 1987; Stark and Redente 1990a). However, plant tissue F concentrations are well below those deemed hazardous to animals. The primary concern associated with F in spent oil shale disposal environments is the potential for this element to leach to groundwater environments. Fluorine is mobile (Stark and

Redente 1986); unlike Mo, the spent oil shale has a capacity to regenerate elevated leachate F concentrations. It is imperative to understand the processes controlling F and Mo aqueous and solid-phase distribution. In order to understand the chemistry of F and Mo in spent oil shale disposal environments it is necessary to predict fate and behavior and assess the effectiveness of proposed mitigation techniques (e.g., recarbonation).

Several methods have been used to identify Mo- and F-bearing solid phases in spent oil shale. Essington (1989a), using a selective sequential extraction technique, concluded that Mo was associated with chemically resistant, nonextractable solid phases (Fe oxides, Fe sulfides, and aluminosilicates). These results were supported by Spackman and Essington (1988). They statistically examined the partitioning of elements into spent oil shale density separates and concluded that Mo was associated with Fe-bearing minerals. In contrast, equilibrium solubility measurements have suggested that the precipitation of powellite (CaMoO_4) and fluorite (CaF_2) control the leachate concentrations of Mo and F (Saether and Runnells 1980; Stollenwerk and Runnells 1981; Essington and Spackman 1986; Essington et al. 1987; Essington 1987; Reddy and Hasfurther 1989).

One problem associated with spent oil shale solubility studies is the lack of relevant thermodynamic data necessary to describe aqueous speciation. Essington (1990a, 1991) and Essington and Huntington (1990) determined the ion association constants for the formation of CaMoO_4^0 , MgMoO_4^0 , KMoO_4^- , and NaMoO_4^- and the equilibrium solubility of powellite. Application of these data to geochemical models suggested that spent oil shale leachates were highly undersaturated with respect to powellite and resulted in the conclusion that powellite did not control soluble Mo concentrations. Essington (1990a) reported that the sum of the concentrations of alkaline earth and alkali metal molybdate ion pairs accounted for more than 50% of the total soluble Mo in spent oil shale leachates. This finding showed the significance of ion pairs and the potential errors involved in data interpretations when they are not considered. Essington (1990a) also noted that an equilibration period greater than 28 days was required to obtain constant ion activity products in the powellite solubility studies. However, few of the studies cited above used equilibration times approaching 28 days.

The equilibrium solubility method, despite its shortcomings, can provide useful information on the phases controlling solution chemistry. Historically, spent oil shale equilibrium solubility studies have been performed using fresh solid waste materials to assess Mo and F leachate and mineralogical character. However, these studies do not examine solubility relationships as a function of exposure in a weathering environment. Thus, changes in Mo and F solid-phase chemistry with spent oil shale weathering have not been adequately assessed.

There are three objectives to the present study: (1) to use the humidity cell simulated weathering technique to examine combusted western (Green River Formation) and eastern (New Albany Shale) oil shale mineralogy and leachate chemistry as a function of relative time in a nonequilibrium, unsaturated leaching environment; (2) to reexamine the

an overall understanding of the Mo and F solubility relationships in spent oil shale; and (3) to examine the solubility relations of Mo and F, in Green River Formation oil shale, as a function of relative time in an equilibrium leaching environment using a simulated weathering technique.

MATERIALS AND METHODS

Sample Preparation

Green River Formation oil shale from the Piceance Creek Basin was obtained from the Exxon Colony Oil Shale Mine near Parachute, Colorado. Clegg Creek Member, New Albany Shale was obtained from the Knieriem quarry located approximately 16 miles south of the Ohio River at Louisville, Kentucky. The mineralogy (Table 1) of the Green River Formation oil shale and the New Albany Shale is described by Miknis and Robertson (1987).

Table 1. Mineralogy of Green River Formation Oil Shale and New Albany Shale (modified from Miknis and Robertson 1987)

Green River Formation	New Albany Shale
Quartz	Quartz
Ankerite	Illite
Calcite	Smectite
Dawsonite	Pyrite
Feldspar	Feldspar
Mg-siderite	Kaolinite/Chlorite
Pyrite	Calcite

Minerals listed in decreasing order of abundance

The combusted Green River Formation oil shale (designated CW) was produced in a fluidized-bed reactor using CO₂ as the retort gas, air as the combustion gas, an average retorting shale bed temperature of 570°C (1058°F), an average combustion bed temperature of 610°C (1130°F) and a residence time of 5 minutes. The combusted New Albany Shale (designated CE) was also produced in a fluidized-bed reactor using CO₂ and air as the retort and combustion gases, an average retort bed temperature of 580°C (1076°F), an average combustion bed temperature of 640°C (1184°F), and a residence time of 5 minutes (Merriam et al. 1987). A second processed Green River Formation oil shale sample (designated LR) was obtained from the Rio Blanco Oil Shale Company Inc., Tract C-a, Colorado. The retorted oil shale was produced by the Lurgi-Ruhrgas process using air as the process gas and a temperature of approximately 530°C (986°F). Rammner (1982) describes the Lurgi-Ruhrgas process for the retorting of oil shale.

Simulated Laboratory Weathering

The spent oil shale samples were very friable and, when necessary, were lightly ground to pass a 2-mm sieve and riffled to obtain representative sample materials for the study. For the laboratory weathering experiment, subsamples of the CW, CE, and LR materials were subjected to nonequilibrium weathering using the humidity cell technique (Caruccio 1968; Sullivan et al. 1987b). Duplicate, 1.0-kg samples of each spent oil shale were sealed in Teflon-coated containers. Dry air was passed over the samples for three days. Humidified air was then passed over the samples for four days. On the seventh day, 1.0 L of Milli-Q reagent-grade, Type I water (Millipore Corp., Bedford, MA) was added to the spent oil shale samples and allowed to react for one hour. Type I water was added to the system to maintain a 1:1 solid-to-solute extraction ratio. The solution and solid phases were separated by sequential vacuum filtration through Whatman 42 filter paper (Whatman, Maidstone, England) and a 0.45- μ m Millipore filter (Millipore Corp., Bedford, MA). The leachates were subjected to chemical analysis, and the solids were returned to the reaction vessel and allowed to dry at room temperature. Humidified air was then passed over the samples for seven days and the extraction was repeated. The seven-day weathering cycle continued for 18 weeks.

F and Mo solubility relationships were evaluated by subjecting the CW and LR materials to equilibrium laboratory weathering using a modified batch technique. Triplicate, 250.0-g samples of each spent oil shale and 0.5 L of Milli-Q reagent-grade, Type I water (Millipore Corp., Bedford, MA) were placed in 1.0-L polypropylene bottles. Each bottle was equipped with a 2-hole Neoprene rubber stopper. A glass tube was placed through one hole to disperse humidified air to the bottom of the bottle. A glass tube was placed through the second hole for exhaust. The bottles were tightly stoppered and placed in a $25.0 \pm 0.1^\circ\text{C}$ ($77 \pm 1.8^\circ\text{F}$) water bath. Humidified air was bubbled through the reaction vessels for a 28-day equilibration period. During this period, the bottles were manually agitated 5 minutes per day, and the weight of each bottle was monitored and maintained by the addition of Type I water.

Upon completion of the first equilibration cycle, the solution and solid phases were separated by sequential vacuum filtration through Whatman 42 filter paper and a 0.45- μ m membrane filter. The leachates were analyzed, and the solids were air-dried and returned to the reaction vessels. A sufficient volume of Type I water was added to each bottle to make a 1:2 solid-to-solute ratio. The suspensions were vigorously shaken, stoppered, and humidified air was bubbled through the reaction vessel for a second 28-day equilibration period. At the completion of the second cycle, the leachates were sampled as before, the solids returned to the reaction vessels, and the cycle repeated. The spent oil shale samples were weathered for a total of six equilibration cycles.

Chemical Analysis

The methods of chemical analysis for both the laboratory weathering and the Mo and F solubility relationship experiments were similar.

Chemical Analysis

The methods of chemical analysis for both the laboratory weathering and the Mo and F solubility relationship experiments were similar. After separation and before filtration, leachate pH was determined with a standardized combination pH electrode (pH 7 and 10) and a Corning model 255 pH/ion meter (Corning Science Products, Corning, NY). Leachate electrical conductivity (EC) was determined with a YSI model 3403 conductivity cell ($K = 1.0 \text{ cm}^{-1}$) and a YSI model 34 conductivity resistance meter (YSI, Yellow Springs, OH). After filtration, the leachate samples were split, and subsamples were analyzed for Al, B, Ba, Ca, Fe, K, Li, Mg, Mn, Mo, Na, Si, Sr, V, and Zn by inductively coupled plasma (ICP) using a Jarrell-Ash 1100 spectrometer (Jarrell-Ash Corp., Franklin, MA). In the solubility relationship study, only Al, Ca, K, Mg, Mo, Na, and Si were analyzed by ICP. Subsamples for ICP analysis were predigested by refluxing in HNO_3 . Standard solutions for ICP analysis were prepared from ultrahigh-purity-grade chemicals or metals and verified against EPA7 and EPA19 reference solutions. During the study, the prepared standards were within $\pm 10\%$ of the reference solutions. Spectral interference and background correction factors were verified by spike recovery analysis and analysis of diluted samples. Spiked and diluted samples were within $\pm 10\%$ of the sample results.

The subsamples were also analyzed by ion chromatography for F, Cl, NO_3 , CO_3 , SO_4 , and S_2O_3 with a Dionex model 4040i dual-channel ion chromatograph (Dionex Corp., Sunnyvale, CA). Standard solutions were prepared using ultrahigh-purity-grade salts. For any given ion, the coefficient of variation for multiple analyses of a single sample was within $\pm 10\%$.

Mineralogical Analysis

Subsamples of the weathered spent oil shales were obtained from the humidity cells prior to extractions 2, 5, and 8. Bulk mineralogy of the spent oil shale and weathered spent oil shale samples was determined by X-ray diffraction analysis (XRD) using a Scintag PAD V diffractometer (Scintag, Santa Clara, CA). X-ray analysis was performed on randomly oriented samples using Ni-filtered $\text{CuK}\alpha$ radiation at 45 kV and 40 mA. Samples were scanned from 2 to 65° at $2\theta \text{ min}^{-1}$. The XRD profiles were interpreted by manual interaction with Scintag software containing Joint Committee on Powder Diffraction Standards files. The chemical formulas of minerals discussed in the text are listed in the Appendix.

Geochemical Model Analysis

The activities of F^- and MoO_4^{2-} were predicted using the model GEOCHEM (Sposito and Mattigod 1980). The pH and total metal and anion concentrations of extracts from weathered spent oil shale were used as input data for the geochemical code. The code calculates the free ionic and ion pair species distributions by numerically solving a set of coupled nonlinear algebraic equations by successive iterations. Each equation relates total soluble element concentrations to free ionic and ion pair species concentrations using the appropriate conditional stability constants and stoichiometry. Ionic strength corrections and

species activity calculations were performed using the Davies or the Debye-Hückel limiting law equations for charged species and the Setchenow-Harned-Owen equation for neutral species. The GEOCHEM thermodynamic data base was altered to include species important in highly alkaline solutions (e.g., HSiO_4^{3-} , SiO_4^{4-}), soluble molybdate species (NaMoO_4^- , CaMoO_4^0 , MgMoO_4^0), and critically evaluated data. The pertinent chemical reactions and association constants used in the model computations are listed in Table 2.

The activities of Ca, F, and MoO_4 predicted by GEOCHEM were used to calculate ion activity product (IAP) values for fluorite (CaF_2) and powellite (CaMoO_4). For CaF_2 and CaMoO_4 , the IAP is equal to $(\text{Ca}^{2+})(\text{F}^-)_2$ and $(\text{Ca}^{2+})(\text{MoO}_4^{2-})$, respectively. The IAP values were compared to the equilibrium solubility product constants (K_{sp}) for powellite ($\log K_{\text{sp}} = -7.86$; Essington and Huntington 1990) and fluorite ($\log K_{\text{sp}} = -10.96$; Nordstrom and Jenne 1977) to identify the saturation status of the spent oil shale solutions. Undersaturation is predicted when the calculated IAP value is less than K_{sp} and suggests that the mineral will dissolve if present. Supersaturation is predicted when the calculated IAP value is greater than K_{sp} and suggests that the mineral will precipitate. When the calculated IAP is equal to the K_{sp} and a condition of equilibrium can be established, the mineral is predicted to be present and controlling the solution activities of its component ions.

In addition to the data generated from the spent oil shale laboratory weathering extractions, several data sets associated with spent oil shale solutions were chosen from the literature for ion association model examination. The data sources were Saether and Runnells (1980), Stollenwerk and Runnells (1981), Esmaili et al. (1985), Essington and Spackman (1986 and 1988), Reddy and Lindsay (1986), Reddy et al. (1986), Essington et al. (1987), Reddy and Hasfurther (1989), and Essington (1990a). The chemical characteristics of these solutions were input to the GEOCHEM code. To account for the formation of soluble molybdate complexes and provide comparable results across all data sets, it was necessary to reevaluate the data in the literature using a single thermodynamic data base.

RESULTS AND DISCUSSION

Mineralogy

The mineralogies of the combusted oil shale samples as a function of weathering cycles are listed in Table 3. Before weathering, the mineralogy of the CW sample was dominated by silicate (quartz, plagioclase), alkaline earth oxide (lime, periclase), and carbonate (calcite, ankeritic dolomite) minerals. Pyrite, present in the raw oil shale, was converted to hematite (as was ankeritic dolomite), and the SO_2 released during the combustion process was captured by calcite to form anhydrite (Smith et al. 1978; Williamson et al. 1980).

Table 2. Chemical Reactions and Association Constants used by GEOCHEM^a

Reaction	log K
$\text{Ca}^{2+} + \text{CO}_3^{2-} = \text{CaCO}_3^0$	3.2
$\text{Ca}^{2+} + \text{H}^+ + \text{CO}_3^{2-} = \text{CaHCO}_3^+$	11.4
$\text{Ca}^{2+} + \text{SO}_4^{2-} = \text{CaSO}_4^0$	2.3
$\text{Ca}^{2+} + \text{F}^- = \text{CaF}^+$	1.1
$\text{Ca}^{2+} + \text{H}^+ + \text{H}_2\text{SiO}_4^{2-} = \text{CaH}_3\text{SiO}_4^+$	14.4
$\text{Ca}^{2+} + 2\text{H}^+ + 2\text{H}_2\text{SiO}_4^{2-} = \text{Ca}(\text{H}_3\text{SiO}_4)_2^0$	35.6
$\text{Ca}^{2+} + \text{MoO}_4^{2-} = \text{CaMoO}_4^0$	2.6
$\text{Ca}^{2+} + \text{H}_2\text{O} = \text{CaOH}^+ + \text{H}^+$	-12.6
$\text{Mg}^{2+} + \text{CO}_3^{2-} = \text{MgCO}_3^0$	2.9
$\text{Mg}^{2+} + \text{H}^+ + \text{CO}_3^{2-} = \text{MgHCO}_3^+$	11.4
$\text{Mg}^{2+} + \text{SO}_4^{2-} = \text{MgSO}_4^0$	2.2
$\text{Mg}^{2+} + \text{F}^- = \text{MgF}^+$	1.8
$\text{Mg}^{2+} + \text{H}^+ + \text{H}_2\text{SiO}_4^{2-} = \text{MgH}_3\text{SiO}_4^+$	14.6
$\text{Mg}^{2+} + 2\text{H}^+ + 2\text{H}_2\text{SiO}_4^{2-} = \text{Mg}(\text{H}_3\text{SiO}_4)_2^0$	31.6
$\text{Mg}^{2+} + \text{MoO}_4^{2-} = \text{MgMoO}_4^0$	3.0
$\text{Mg}^{2+} + \text{H}_2\text{O} = \text{MgOH}^+ + \text{H}^+$	-11.8
$\text{K}^+ + \text{CO}_3^{2-} = \text{KCO}_3^-$	0.6
$\text{K}^+ + \text{SO}_4^{2-} = \text{KSO}_4^-$	0.9
$2\text{K}^+ + \text{SO}_4^{2-} = \text{K}_2\text{SO}_4^{0-}$	1.5
$\text{K}^+ + \text{F}^- = \text{KF}^0$	-0.8
$\text{Na}^+ + \text{CO}_3^{2-} = \text{NaCO}_3^-$	0.6
$\text{Na}^+ + \text{SO}_4^{2-} = \text{NaSO}_4^-$	1.1
$2\text{Na}^+ + \text{SO}_4^{2-} = \text{Na}_2\text{SO}_4^0$	1.5
$\text{Na}^+ + \text{F}^- = \text{NaF}^0$	-1.0
$\text{Na}^+ + \text{MoO}_4^{2-} = \text{NaMoO}_4^-$	1.1
$\text{Na}^+ + \text{H}_2\text{O} = \text{NaOH}^0 + \text{H}^+$	-14.2
$\text{H}^+ + \text{CO}_3^{2-} = \text{HCO}_3^-$	10.3
$\text{H}^+ + \text{H}_2\text{SiO}_4^{2-} = \text{H}_3\text{SiO}_4^-$	13.3
$\text{H}_2\text{SiO}_4^{2-} = \text{HSiO}_4^{3-} + \text{H}^+$	-9.9
$\text{H}_2\text{SiO}_4^{2-} = \text{SiO}_4^{4-} + 2\text{H}^+$	-23.0

^a Only significant complexes are listed here.

Table 3. Mineralogy of Nonweathered and Weathered Processed Oil Shale Samples

Mineral	Weathering Cycle			
	Nonweathered	1	4	7
<u>Peak Intensity</u>				
Combusted Western Oil Shale				
Anhydrite	M	0	0	0
Ankeritic Dolomite	W	W	W	W
Calcite	W	M	S	S
Ettringite	0	M	0	0
Gypsum	0	0	0	VW
Hematite	VW	VW	VW	W
Lime	M	0	0	0
Na-plagioclase	M	W	M	M
Periclase	W	VW	0	0
Quartz	VS	VS	VS	VS
Lurgi-Ruhrgas				
Analcime/Wairakite	W	W	W	W
Anhydrite	VW	0	0	0
Ankeritic Dolomite	M	M	M	M
Calcite	S	VS	VS	VS
Ettringite	0	VW	0	0
Hematite	VW	VW	VW	VW
Na-plagioclase	W	W	W	W
Periclase	W	0	0	0
Quartz	VS	S	S	3
Combusted Eastern Oil Shale				
Gypsum	0	VW	VW	VW
Hematite	W	W	W	W
Illite	W	W	W	W
Orthoclase	VW	VW	VW	VW
Quartz	VS	VS	VS	VS

Relative peak intensities: VS = 100%, S = 99-50%, M = 49-20%, W = 19-10%, VW <10%, 0 = none detected.

The mineral assemblage in the CW sample is similar to assemblages in Green River Formation oil shale samples retorted and combusted under similar conditions. For combustion temperatures ranging from 600 to 800°C (1112 to 1472°F), minerals identified in processed Green River Formation oil shale samples include quartz, calcite, periclase, dolomite, analcime (wairakite), akermanite (gehlenite), augite, diopside, pyrite, pyrrhotite, lime, anhydrite, hematite, and feldspars (Park et al. 1979; Mason et al. 1984; Smith et al. 1978; Campbell and Burnham 1978; Williamson et al. 1980). Akermanite, augite, analcime, pyrite, pyrrhotite, and diopside were not detected in the CW sample.

During the first weathering cycle, lime and anhydrite dissolved, and the solubilized Ca and SO₄ precipitated as calcite and a Ca-rich, Al-poor ettringite, $\text{Ca}_{6.32}\text{Al}_{1.05}(\text{SO}_4)_{2.27}(\text{SiO}_4)_{0.36}(\text{OH})_{9.83} \cdot 26\text{H}_2\text{O}$ (Essington 1990b). A decrease in periclase XRD peak intensities was also apparent. As weathering increased, ettringite and periclase dissolved. Calcium and SO₄, solubilized by the dissolution of ettringite, precipitated as calcite and gypsum.

An XRD-detectable, Mg-bearing mineral did not form during CW weathering. Reddy and Lindsay (1986) and Reddy et al. (1986) examined the leachate chemistry and mineralogy of a processed and a recarbonated processed Green River Formation oil shale and found that Mg activities in spent oil shale leachates were controlled by Mg-silicates (clinoenstatite and diopside before recarbonation, and antigorite after). They further report that XRD results substantiated the occurrence of these minerals. In the present study, the occurrence of clinoenstatite, diopside, or antigorite in the nonweathered and weathered CW samples could not be resolved because the XRD peaks used to identify these Mg silicates coincided with those of calcite, plagioclase, gypsum, and ankeritic dolomite.

The mineralogy of the LR processed oil shale, also produced from Green River Formation oil shale, was similar to that of the CW sample (Table 3). However, it is apparent that the LR process temperature was lower than that used to produce the CW sample, resulting in a slightly different mineral assemblage. Process temperatures were not sufficient to produce detectable quantities of lime or decompose analcime. Further, the LR sample contained lesser amounts of periclase and anhydrite and greater amounts of calcite compared with the CW sample. This observation is consistent with lower combustion temperatures. However, the process temperature was sufficient to produce XRD-detectable hematite from pyrite and ankeritic dolomite.

The weathering reactions of the LR sample were also similar to those of the CW sample (Table 3). During the first weathering cycle, periclase and anhydrite dissolved, and solubilized Ca and SO₄ precipitated as ettringite and calcite. Mg-bearing minerals were not detected in the weathered LR samples. With additional weathering, ettringite dissolved, and solubilized Ca precipitated as calcite.

The mineralogy of the combusted New Albany Shale sample (CE) is similar to that of the raw oil shale (Tables 1 and 3). Pyrite is

thermally altered to hematite (Smith et al. 1978; Williamson et al. 1980). Gypsum was the only weathering product detected by XRD during the weathering study. With the exception of gypsum, the remaining mineral assemblage was not altered during the weathering study. The appearance of gypsum in processed eastern oil shale weathered in field lysimeters has been predicted from solubility data (Essington 1989b; Robl 1989). Thus, the occurrence in the laboratory-weathered samples substantiates the presence of gypsum in a field disposal environment.

Leachate Chemistry

Figure 1 illustrates the changes in processed oil shale leachate pH and EC as a function of weathering cycle. The high alkalinity of CW and LR samples, primarily resulting from the dissolution of lime and periclase, was mobile and readily leached during the initial weathering cycles. After five weathering cycles, CW and LR leachate pH values stabilize between 8.5 and 9, suggesting that calcite influenced leachate of pH. The reduction in leachate pH for spent Green River Formation oil shale leachate has been observed in field lysimeters (Garland et al. 1979; Richardson et al. 1981; Stark and Redente 1986). Garland et al. (1979) suggest that the reduction in leachate pH was due to oxidation of reduced sulfur species, and to a lesser extent, recarbonation (absorption of CO_2). Reddy et al. (1986) viewed recarbonation as the dominant process responsible for the reduction in spent oil shale leachate alkalinity. Because reduced sulfur species were not detected in the humidity cell leachates, the reduction of CW and LR leachate pH values probably resulted from the combined effects of recarbonation and leaching.

The pH of processed eastern oil shale leachates is dependent on the pyrite content of the solid waste product, which in turn is dependent on oil shale processing parameters (heating rate and maximum temperature) (Williamson et al. 1980; Cisler and Koppenaal 1982; Paciorek et al. 1983; Tian and Ehmann 1984). Acidic spent oil shale leachates are produced when the oil extraction process does not thermally decompose pyrite. The pH values of CE leachates tended to fluctuate between 7.5 and 8.5 during this study. This shows that the combustion process was sufficient to decompose pyrite (to hematite) and neutralize the acid production potential of the waste material.

The humidity cell leachate results for the CE sample were different from those reported by Sullivan et al. (1987c) for retorted and combusted New Albany Shale. The pH of the CE materials was constant during the weathering study, even though the material had a negative acid-neutralizing capacity (CE acid-base account of -2.3 ton CaCO_3 /1000 ton of spent oil shale, unpublished data, M.E. Essington). Sullivan et al. (1987c) noted a continual decrease in leachate pH through 20 weathering cycles. Final leachate pH values of approximately 2.5 and 5 were achieved for the retorted and combusted New Albany Shale samples, respectively, even though the New Albany Shale combustion process used lime as an additive that resulted in an acid base account of +224.7 ton CaCO_3 /1000 ton waste.

Figure 1. pH (a) and EC (b) of Humidity Cell Leachates from Combusted (CW) and Lurgi-Ruhrgas Processed (LR) Green River Formation Oil Shale and Combusted New Albany Shale (CE)

Soluble salts in processed oil shale are readily removed with leaching (Fransway and Wagenet 1981; Stollenwerk and Runnells 1981; Stark and Redente 1986). A general decrease in salt content, determined by EC measurements, was also observed for the CW, LR, and CE processed oil shale leachates. Leachates from the initial weathering cycle of CW and CE were highly saline in comparison with the salinity of the initial LR leachates. Following the first weathering cycle and the removal of the highly soluble salts, the EC of the CW leachates remained constant through the sixth weathering cycle and then a general decreasing trend was observed. For the CE samples, leachate EC consistently decreased with weathering. The EC of the LR leachates also remained relatively constant through the sixth weathering cycle, before a consistent decrease was observed. Reduction of leachate EC to $<2 \text{ dS m}^{-1}$ required 13 weathering cycles for CE, 8 cycles for LR, and 9 cycles for CW.

Initially, relatively low solubilities of Mg, Ca, Sr, Li, and B were measured in the CW leachates (Figure 2). Depressed concentrations of these constituents may be due to the slow kinetics of dissolution or to the relative stability of the solid phases (lime and periclase) under the highly alkaline conditions. As alkalinity was removed (or neutralized by CO_2 absorption) and pH decreased, the potential for oxide dissolution increased, resulting in higher concentrations of these elements. As leaching continued, leachate concentrations decreased. Relatively low initial CO_3 concentrations were measured. High alkalinity and an abundance of soluble Ca resulted in the precipitation of absorbed CO_2 . As pH and soluble Ca decreased, CO_3 concentrations increased and stabilized, as influenced by calcite solubility.

For the remaining parameters SO_4 , Na, K, Cl, Si, F, and Mo, the highest CW leachate concentrations occurred in the initial extracts. Leachate concentrations of these constituents generally decreased with the number of weathering cycles. The behavior of Mo, B, and F in CW and LR materials during weathering is similar to that observed by Stollenwerk and Runnells (1981). The leachate concentrations of Mo rapidly decreased with leaching. The leachate concentrations of F and B were reduced with leaching. However, F concentrations remained relatively high.

Leachates from the LR samples were less alkaline initially than those of CW, because the concentrations of alkaline earth oxides were lower. For Ca, Sr, and B, the relatively low initial concentrations observed in CW leachates were not detected in the LR leachates (Figure 3). However, in LR leachates Mg, Li, and CO_3 concentrations responded to weathering in a fashion similar to those species in the CW leachates.

In relation to XRD mineralogy, initially high pH values for the CW and LR samples were due to the dissolution of lime and periclase. Constituents released from the dissolution of these and other soluble minerals, such as Ca, Al (0.53 and 0.40 mmol L^{-1} in cycle 1 and 2 leachates, respectively), and SO_4 reprecipitated as ettringite, which is stable under the highly alkaline conditions (Essington 1990a). As the alkalinity was leached from the samples, ettringite became unstable, and the solubilized Ca and SO_4 precipitated as calcite and gypsum. The

Figure 2. Chemical Characteristics of Humidity Cell Leachates from Combusted Green River Formation Oil Shale

Figure 3. Chemical Characteristics of Humidity Cell Leachates from Lurgi-Ruhrgas Processed Green River Formation Oil Shale

dissolution of these minerals then controlled the leachate concentrations of Ca and SO_4 . Under the highly alkaline conditions, CO_2 is absorbed and rapidly precipitates as calcite (Reddy et al. 1986). As leaching increased and pH was reduced, CO_3 concentrations leveled off and were controlled by calcite. Magnesium released by the dissolution of periclase did not appear to reprecipitate as predicted by Reddy et al. (1986) and Reddy and Lindsay (1986). The released Mg remained soluble and was leached from the processed oil shale. The concentrations of the highly soluble salts, Na, SO_4 , and K, diminished with weathering cycles.

With increased weathering, the CE leachate concentrations of soluble constituents generally decreased (Figure 4). Further, leachate concentrations of Si increased and CO_3 leachate concentrations remained relatively constant with weathering. Leachate concentrations of Mo and B were initially elevated compared with the CW and LR leachates. However, the CE leachate concentrations of these elements and F rapidly decreased with weathering. The conversion of pyrite to hematite during the combustion process has eliminated the acid drainage potential of the processed New Albany Shale.

Batch Equilibrium Solubility Relationships

The use of chemical thermodynamics to describe the status of an environment has been practiced for a number of years. In a natural or waste affected environment, the number of reactions that must be considered to characterize solution-phase and solid-phase chemistry can be quite large (Baham 1984). Efforts to account for these many reactions have resulted in the development of computer equilibrium models (or codes). These geochemical codes, which have been extensively reviewed and compared (Nordstrom et al. 1979; Baham 1984; Sposito 1984), consider many of the attributes desirable in a geochemical code (Jenne 1979; Mattigod et al. 1981; Mattigod and Page 1983). The codes use ion association constants, solubility product constants, and analytical concentration data to predict the distribution of an element between free anionic or cationic species and ion pairs and solid phases. Although the ion association model has a firm theoretical basis, the computer codes used to perform the model computations have a number of inherent shortcomings. Principal among these are incomplete data on solubility-controlling solids, such as stoichiometry, crystallinity, and thermodynamic properties; inability to describe thermodynamically adsorption/desorption and ion exchange reactions; lack of thermodynamic data to characterize ion pair and complex ion formation reaction involving metal ions and organic ligands; lack of accurate thermodynamic data for reduction-oxidation reactions; and variations in the thermodynamic data sets used by the different geochemical computer codes (Jenne 1979).

The ion association model can be used to indirectly identify solid phases that control leachate chemistry. The method consists of comparing the predicted ion activity products (IAP) in spent oil shale solutions with the solubility product constants (K_{sp}) for various

Figure 4. Chemical Characteristics of Humidity Cell Leachates from Combusted New Albany Shale

minerals. Assuming equilibrium exists, the mineral whose K_{sp} is equal to the predicted IAP is assumed to be present and controlling ionic activities in the spent oil shale solution. Basic requirements for obtaining valid results from the application of the equilibrium solubility method are (1) the condition of equilibrium between mineral and aqueous components; (2) all minerals that are likely to be present must be considered, and their K_{sp} values must be known; (3) unit activity of the mineral phases; (4) accurate computation of ion activities and IAP values; and (5) knowledge regarding the kinetics of the various mineral dissolution and precipitation reactions (Mattigod et al. 1981). The equilibrium solubility method has been extensively applied to indirectly identify mineral phases that may control spent oil shale solution chemistry (Saether and Runnells 1980; Stollenwerk and Runnells 1981; Essington and Spackman 1986 and 1988; Reddy and Lindsay 1986; Reddy et al. 1986; Essington et al. 1987; Essington 1987; Reddy and Hasfurther 1989; Reddy et al. 1989; Essington 1990a).

The powellite IAP values predicted using GEOCHEM for spent western oil shale data found in the literature are highly variable, particularly at short reaction times (Figure 5). In general, leachates from spent western oil shale are undersaturated with respect to powellite. However, at short reaction times, a number of solutions approach saturation with respect to powellite. Comparable powellite IAP and K_{sp} values at these short reaction times has been used as indirect evidence that powellite is present and controlling Mo concentrations (Reddy and Hasfurther 1989). However, Essington (1990b) noted that a reaction time of 28 days is required to attain powellite solubility equilibrium in KNO_3 solutions. As reaction times increase, spent oil shale leachates become increasingly undersaturated with respect to powellite. This suggests that Mo concentrations are not controlled by powellite solubility.

The fluorite IAP values are also highly variable, particularly at short reaction times (Figure 6). In general, the batch solutions are supersaturated with respect to fluorite at short reaction times. As equilibration times increase, the spent oil shale solutions approach saturation with respect to fluorite. These data are indirect evidence that F in spent western oil shale may reside in fluorite and also show that soluble F equilibrium with fluorite may require long equilibration times. The scattering associated with the powellite and fluorite IAP values can be attributed to the many different process parameters used in the production of the spent oil shale samples. Process heating rate, maximum temperature and duration, and gas composition will directly influence the mineralogical composition of the spent oil shale (Campbell and Burnham 1978; Park et al. 1979; Williamson et al. 1980), which in turn influences leachate composition. The spent oil shales examined (Figures 5 and 6) were generated using a Paraho (indirect and direct retort) or a combustion process (fluidized-bed, TOSCO, Lurgi-Ruhrgas), which produce solid waste materials having similar mineralogical and chemical character.

Figure 5. Powellite Ion Activity Product Values as a Function of Elapsed Time

Simulated Equilibrium Weathering

Processed oil shale leachate pH, EC, and elemental composition are listed in Table 4 as a function of the weathering cycle. These results are similar to those reported above for the nonequilibrium weathering of CW and LR samples. Leachates from the LR samples are initially less alkaline than those of CW, which have a higher alkaline earth oxide content. A general decrease in salt content, determined by EC measurements, is also detected in the processed oil shale leachates. Initially, the leachates have relatively low concentrations of Mg and Ca. The depressed concentrations of these elements may be due to the slow kinetics of dissolution, or to the relative stability of the solid phases (lime and periclase) under the highly alkaline conditions. As alkalinity is removed or neutralized and pH decreases, the potential for oxide dissolution increases, resulting in increased concentrations of these elements.

The highest leachate concentrations for SO_4 , CO_3 , Na, K, Cl, and Si were in the initial extracts. Leachate concentrations of these elements generally decreased with the number of weathering cycles. The concentration of Mo in CW and LR leachates also decreased with leaching. Leachate concentrations of F were reduced with leaching; however, F concentrations remain relatively high, particularly in the CW sample. During the initial weathering cycle the spent oil shale leachates were undersaturated with respect to powellite (Figure 7). The second cycle and remaining LR leachates were saturated with respect to powellite. The CW leachates approached saturation with respect to powellite during cycles 5 and 6. These results suggest that powellite will control Mo chemistry in spent oil shale leachates as equilibrium weathering proceeds. Thus, the prediction of Mo fate and behavior in a weathering spent oil shale environment can be accomplished using equilibrium models.

The spent oil shale leachates approached near-saturation with respect to fluorite during the initial weathering cycles (Figure 8). However, as equilibrium weathering continued, the leachates become supersaturated with respect to fluorite. These results suggest that fluorite is not controlling the concentration of F in the spent oil shale leachates. The results further suggest that the F released during the weathering of spent oil shale may be leached to potentially affect groundwater environments. These results also show that the prediction of F chemistry in a spent oil shale disposal environment can not be based on fluorite solubility relationships. The supersaturated conditions show that there is a potential for fluorite to precipitate. However, kinetic constraints may limit fluorite precipitation.

The interpretation of spent oil shale solubility results will depend upon the method used to obtain equilibrium leachates. The results of the equilibrium studies show that the batch results are comparable to those obtained for the initial cycle of the simulated equilibrium weathering study. Spent oil shale batch equilibrium extracts were undersaturated with respect to powellite and saturated with respect to fluorite.

Table 4. Mean Chemical Characteristics of Triplicate Samples of Simulated Equilibrium Weathering Leachates

Cycle	pH	EC	Al	Ca	K	Mg	Mo	Na	Si	CO ₃	Cl	F	SO ₄
<div> <div>dS m⁻¹</div> <div>-----mmol L⁻¹-----</div> <div>Combusted Oil Shale</div> </div>													
1	12.07	14.38	2.172	0.224	12.25	<0.001	0.094	123.7	5.946	9.482	1.376	0.565	51.13
2	11.61	10.20	0.322	1.013	7.954	0.021	0.065	80.60	0.775	3.966	0.496	0.384	22.73
3	11.27	7.63	0.288	2.602	8.356	0.213	0.045	66.52	0.524	2.595	0.275	0.436	23.77
4	9.69	5.69	0.136	0.928	9.156	0.413	0.034	67.07	0.057	0.940	0.162	0.593	22.10
5	10.61	5.54	0.099	6.554	13.25	0.124	0.040	78.60	0.275	0.528	0.211	0.421	29.10
6	9.86	4.01	0.065	8.733	9.156	0.236	0.026	55.94	0.045	0.325	0.119	0.387	24.50
<div> <div></div> <div>-----Lurgi-Ruhrgas-----</div> <div></div> </div>													
1	11.44	7.46	0.067	0.767	9.507	0.012	0.055	70.32	0.129	6.166	2.042	0.704	40.77
2	10.75	6.70	0.027	4.484	9.584	<0.001	0.037	54.95	0.769	1.188	0.455	0.262	18.74
3	9.85	5.01	0.054	9.853	7.727	0.157	0.020	33.86	0.354	1.173	0.555	0.595	39.56
4	8.95	3.45	<0.001	12.48	5.542	1.724	0.015	22.13	0.285	0.383	0.197	0.329	15.82
5	9.41	4.20	0.008	11.79	4.755	0.844	0.013	14.47	0.256	<0.02	0.181	0.221	13.92
6	9.26	3.08	0.004	11.66	4.079	2.897	0.013	9.917	0.243	<0.02	0.111	0.191	11.48

Figure 7. Powellite Ion Activity Product Values as a Function of Weathering Cycle

Figure 8. Fluorite Ion Activity Product Values as a Function of Weathering Cycle

CONCLUSIONS

The mineralogy of western spent oil shales will change with time. Leachate pH will rapidly decrease from highly alkaline values to pH values controlled by calcite. The leachate concentrations of soluble salts will also decrease. During the initial stages of weathering, the processed western oil shale leachates were dominated by Na, hydroxide, and SO_4 . As weathering continued, Mg, SO_4 , and CO_3 dominated leachate chemistry. Boron should not pose an environmental hazard because leachate concentrations remained low and did not exceed 0.1 mmol L^{-1} . Concentrations of Mo will be elevated initially but will decrease with increased leaching. However, concentrations of F will remain elevated.

The weathering results suggest that alkalinity, salinity, and potentially problematic elements may be readily leached from the CW and LR samples. However, the minimal annual precipitation at potential disposal sites will not allow weathering to proceed. Thus, the leachate chemistry and mineralogy of the spent oil shale materials in the disposal environment will be closely associated with that observed in the initial weathering cycles. These data coupled with the disposal site hydrology also suggest that the potential for off-site contamination may be minimal. Effective revegetation may be accomplished with leaching.

For the CE sample, minor alterations in mineralogy occurred in the disposal environment, primarily the precipitation of gypsum. Potentially hazardous components (Mo, F, and B) will be rapidly removed to influence groundwater and surface water. Similarly, soluble salts will be rapidly removed. In general, Ca and SO_4 dominate the chemistry of CE leachates. The CE samples will reach higher stages of weathering (i.e., a greater number of weathering cycles will occur in the environment) compared with the processed western oil shale samples. This is because the eastern United States has a greater annual precipitation than does the western United States. The results do not suggest that the CE sample is potentially problematic with respect to acid drainage.

GEOCHEM-predicted powellite and fluorite IAP values of spent western oil shale literature data are highly variable. Spent western oil shale leachates are generally undersaturated with respect to powellite. However, in this study, some solutions approached saturation with respect to powellite at short reaction times. Reddy and Hasfurther (1989) determined that powellite was controlling Mo concentrations by comparing powellite IAP and K_{sp} values. However, powellite solubility equilibrium in KNO_3 solutions was noted by Essington (1990) to require a reaction time of 28 days.

This study determined that as reaction times increased, spent oil shale leachates became increasingly undersaturated with respect to powellite, therefore, suggesting that Mo concentrations are not controlled by powellite solubility. Fluorite was generally supersaturated in the batch solutions at short reaction times. However, with increasing reaction time, the spent oil shale solutions approached saturation with respect to fluorite. This evidence indirectly infers

that in spent western oil shale, F concentrations may be controlled by fluorite. Also, these data suggest that long equilibration times may be needed for soluble F to reach equilibrium with fluorite.

Based on these results, we can conclude that a F-bearing mineral in spent oil shale is fluorite. However, because a long equilibrium period is required, F chemistry can not be predicted using solubility models. Similarly, as spent oil shales weather, F chemistry is not controlled by fluorite solubility. Mo concentrations in the batch equilibrations are undersaturated with respect to powellite, suggesting that this solid phase does not control Mo chemistry in fresh spent oil shale. As the spent oil shale weathers, Mo concentrations are apparently controlled by powellite solubility. Thus, the chemistry of Mo in spent oil shale disposal environments which are subject to the slow infiltration of water can be predicted using solubility relationships.

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DISCLAIMER

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

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APPENDIX

CHEMICAL FORMULAS OF MINERALS

<u>Mineral</u>	<u>Chemical Formula</u>
Akermanite	$\text{Ca}_2\text{MgSi}_2\text{O}_7$
Analcime	$\text{NaAlSi}_2\text{O}_6 \cdot \text{H}_2\text{O}$
Anhydrite	CaSO_4
Ankeritic Dolomite	$\text{Ca}(\text{Fe}, \text{Mg})(\text{CO}_3)_2$
Antigorite	$\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$
Augite	$\text{Ca}(\text{Mg}, \text{Al}, \text{Fe})\text{Si}_2\text{O}_6$
Calcite	CaCO_3
Chlorite	$\text{Mg}_2\text{Al}(\text{OH})_6\text{Mg}_3(\text{Si}_3\text{Al})\text{O}_{10}(\text{OH})_2$
Clinoenstatite	MgSiO_3
Dawsonite	$\text{NaAlCO}_3(\text{OH})_2$
Diopside	$\text{CaMg}(\text{SiO}_3)_2$
Dolomite	$\text{CaMg}(\text{CO}_3)_2$
Ettringite	$\text{Ca}_6\text{Al}_2(\text{SO}_4, \text{SiO}_4, \text{CO}_3)_3(\text{OH})_{12} \cdot 26\text{H}_2\text{O}$
Gehlenite	$\text{Ca}_2\text{Al}_2\text{SiO}_7$
Gypsum	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$
Hematite	Fe_2O_3
Illite	$\text{K}_{0.5}(\text{Al}, \text{Fe}, \text{Mg})_3(\text{Si}, \text{Al})_4\text{O}_{10}(\text{OH})_2$
Kaolinite	$\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$
Lime	CaO
Mg-Siderite	$(\text{Fe}, \text{Mg})\text{CO}_3$
Orthoclase	KAlSi_3O_8
Periclase	MgO
Pyrite	FeS_2
Pyrrhotite	Fe_{1-x}S
Quartz	SiO_2
Smectite	$\text{Ca}_{0.2}(\text{Al}, \text{Mg})_2\text{Si}_4\text{O}_{10}(\text{OH})_2$
Wairakite	$\text{CaAl}_2\text{Si}_4\text{O}_{12} \cdot 2\text{H}_2\text{O}$

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