CHEMISTRY OF ALUMINUM AND IRON
MINERALS IN OIL SHALES CONTAINING PYRITE

K.J. Reddy

In

Proceedings of the
1988 Eastern Oil Shale Symposium
Lexington, Kentucky

Sponsored by the

Institute for Mining and Minerals Research,
& Center for Applied Energy Research
University of Kentucky

U.S. Department of Energy

and

Kentucky Energy Cabinet

K.J. Reddy
Wyoming Water Research Center
University of Wyoming
Laramie, Wyoming

Chemistry of Aluminum and Iron Minerals in Oil Shales Containing Pyrite

by

K.J. Reddy
Wyoming Water Research Center
University of Wyoming
Laramie, Wyoming 82071

Abstract: The ability to properly manage acid mine drainage is dependent upon understanding the chemistry of Al and Fe associated with the oxidation of pyritic materials. The objective of this study was to examine the solubility relationships of Al and Fe minerals in oil shales containing pyrite under oxidizing equilibrium conditions. Two eastern oil shales, A New Albany shale (unweathered, 4.6% pyrite) and a Chattanooga shale (weathered, 1.5% pyrite), were used in this study. Oil shale samples were equilibrated with distilled-deionized water from 1 to 180 d(1:1 solid:solution ratio). The equilibrium solutions were filtered and the clear solutions were analyzed for total cations and anions. Ion activities were calculated from total concentrations. Below pH 6.0, depending upon SO_4^{2-} activity, Al^{3+} solubility was controlled by $Al(SO_4)(OH).5H_2O$ for both shales. Initially, Al^{3+} solubility for the New Albany shale showed equilibrium with amorphous $Al(OH)_3(s)$. The pH decreased with time, and Al^{3+} solubility approached equilibrium with $Al(SO_4)-(OH).5H_2O$. Below pH 6.0, Fe^{3+} solubility appeared to be regulated by a basic iron sulfate solid phase with the stoichiometric composistion of $FeOHSO_4(s)$. The results from this study further indicate that the acidity in oil shale waters may be produced from the hydrolysis of Al^{3+} and Fe^{3+} in solution.

Introduction

In a natural aerobic environment there is a potential for iron sulfide compounds to oxidize and to produce acidity. The best example of this natural process is the oxidation of FeS_2 (pyrite) that usually occurs in mining wastes, coal cleaning waste, spoil, and acid sulfate soils (Smith et al. 1974). The oxidation of pyrite in a natural environment is suggested by the following reactions (Stumm and Morgan, 1981):

$$FeS_2 + 7/2\ O_2 + H_2O = Fe^{2+} + 2SO_4^{2-} + 2H^+ \quad (1)$$

$$Fe^{2+} + 1/4\ O_2 + H^+ = Fe^{3+} + 1/2\ H_2O \quad (2)$$

$$Fe^{3+} + 3H_2O = Fe(OH)_3(s) + 3H^+ \quad (3)$$

$$FeS_2 + 14Fe^{3+} + 8H_2O = 15Fe^{2+} + 2SO_4^{2-} + 16H^+ \quad (4)$$
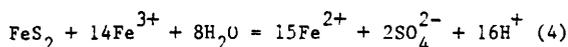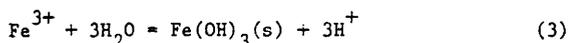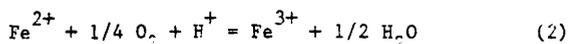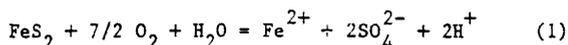
The environmental problems associated with the oxidation of pyrite are well documented (Martin, 1974; Griffin et al. 1980; Wahler, 1978). In order to manage acid mine drainge production effectively, it is important to understand the solubility relationships of Al and Fe minerals in an environment where pyrite will be oxidized.

Several studies have been conducted on the solubility relationships of Al and Fe minerals in acid sulfate soils and acid mine waters (VanBreeman, 1973; Adams and Rawajfith, 1977; Rhodes and Lindsay, 1978; Nordstrom et al. 1979; Nordstrom, 1981; and Filipek et al. 1987). However, none of these studies examined Al and Fe solubilities in oil shales containing pyrite. Thus, the objective of this study was to examine the solubility relationships of Al and Fe minerals in oil shales containing pyrite under oxidizing equilibrium conditions.

Materials and Methods

Two eastern oil shales were used in this study. One is from New Albany and the other is from Chattanooga. The New Albany shale is an unweathered shale that contains 4.6% pyrite, and the Chattanooga shale is a weathered shale that contains 1.5% of pyrite.

Two hundred fifty-gram samples were placed in 500 ml Nalgene plastic bottles. Two hundred fifty milliliters of distilled-deionized H_2O were added to these bottles and tightly capped. Bottles were quipped with a plastic tube through the cap to the bottom of the bottle and supplied with a constant flow of compressed air. Each sample bottle was placed into a water shaker bath at a constant temperature of 25°C. The water samples were shaken at a constant rate of

1988 Eastern Oil Shale Symposium November 30 - December 2, 1988 Institute of Mining and Minerals Research, University of Kentucky

177

60 rpm, and agitated manually three times a week. After reacting for 1, 4, 8, 16, 32, 64, 128, and 180 days of equilibration time, the samples were filtered using 0.45 millipore filters and clear filterates were analyzed for different chemical constituents. pH was measured with a combination electrode. Eh was measured with standard platinum and reference electrodes. Al, As, Ba, Ca, Cd, Co, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, Pb, Sb, Se, Si, Sr, and Zn were analyzed with inductively coupled plasma optical emission spectrometry (ICP-OES). Sulfate was measured with ion chromatography. Chloride was measured with specific ion electrode. Carbonates were determined by titration. All total chemical analyses of equilibrium solutions were coded and speciated with the WATEQFC geo-chemical code (Runnells and Lindberg, 1981). This computer model uses total elemental concentrations, pH, Eh, and temperature of solutions and solves a number of simultaneous chemical reactions to yield equilibrium activities of different ions. From activities, ion activity product (IAP) for different Al and Fe minerals were calculated and compared with log K_{sp} values of Al and Fe minerals to identify minerals controlling the solubility of Al^{3+} and Fe^{3+} activities in acid waters.

RESULTS AND DISCUSSION

Activities of Al^{3+}, Fe^{3+}, Na^+, K^+ and SO_4^{2-}, from the oxidizing equilibration extracts are presented in Table 1. Also included in this table are equilibration time and pH. These data show that for New Albany shale (unweathered with no soluble acidity) extracts the initial pH increased from 5.74 to 7.90 and then decreased to 3.73. However, for the Chattanooga shale (weathered with souble acidity) extracts the pH decreased gradually from 4.62 to 2.44. These data also show that as equilibration time increased the solubilities of Al^{3+} and Fe^{3+} also increased.

Al^{3+} Solubility

The relationship between log IAP versus pH is developed and shown in Figure 1. In this figure log K_{sp} = -17.8 and log K_{sp} = 9.66 corresponds to $Al(SO_4)(OH).5H_2O$ (jurbanite) and $Al(OH)_3$ (amorphous aluminum), respectively. These values were taken from Nordstrom (1982) and Lindsay (1979), respectively.

The ion activity products (IAP's) calculated experimetnaly for each shale extract are plotted in Figure 1 (note: extracts with a poor ion balance are not plotted, see table 1). For the New Albany shale, the initial Al^{3+} activity was in equilibrium with amorphous $Al(OH)_3$. As equilibration time increased, pH decreased, Al^{3+} and SO_4^{2-} activities approached the equilibrium with jurbanite. All IAP's for the Chattanooga shale show equilibrium with jurbanite. In general, above pH of 6.0, the activity of Al^{3+} appears to be controlled by amorphous $Al(OH)_3$ and below pH of 6.0 Al^{3+} activity controlled by jurbanite.

Fe^{3+} Solubility

Acid mine waters resulting from the oxidation of iron sulfides may precipitate a large number of secondary iron phases (Nordstrom, 1982) such as $FeSO_4.7H_2O$ (melanite), $FeSO_4.4H_2O$ (rozenite),

$FeSO_4.6H_2O$ (ferrohexahydrite), $Fe^{2+}Fe_4^{3+}$ $(SO_4)_6(OH)_2$ (copiapite), $(KNa)Fe_3(SO_4)_2(OH)_6$ (jarosite) and $Fe(OH)_3$ (amorphous iron). All of these solid phases are highly soluble except jarosite and amorphous iron. Several studies have been completed on the solubility relationships and precipitation of jarosite in acid mine waters (Nordstrom et al., 1979 and Filipek et al., 1987). These studies observed supersaturation of jarosite. In this study, we also observed that Fe^{3+} activities are not controlled by jarosite.

It is evident from Table 1 that Fe^{3+} activity increases as pH decreases. If Fe^{3+} activity were controlled by a ferric oxide, a one unit decrease in pH would correspond to a 1,000-fold increase in Fe^{3+} activity. Instead, the Fe^{3+} activity increased approximately 10-fold for each unit decrease in pH, except for samples 5 and 6. This suggests that Fe^{3+} activity may be controlled by other ferric iron mineral rather than ferric oxides. Given the pH range between sample 7 (5.11) and sample 15 (3.64), the relationship of log Fe^{3+} + log SO_4^{2-} versus pH gives a regression slope of -1.00. Assuming this slope, the observed relationship can be expressed as follows:

$$\log Fe^{3+} + \log SO_4 + pH = -10.06 \qquad (5)$$

This suggests that equilibrium between dissolved Fe^{3+} and a basic ferric sulfate mineral with the stoichiometric formula of $FeOHSO_4$ as follows:

$$FeOHSO_4 = Fe^{3+} + SO_4^{2-} + OH^- \qquad (6)$$
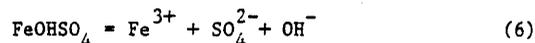
The equilibrium constant for equation (6) is calculated to be $10^{-24.06}$ with an acidic dissociation constant of $10^{-10.06}$ (log K_{sp} = -10.06).

The log K_{sp} of equation (9) was used to develop the relationship between log IAP versus pH for $FeOHSO_4$ in Figure 2. The log K_{sp} = -4.89 for amorphous iron ($Fe(OH)_3$) taken from Ball et al. (1981) is also included in Figure 2 and the experimentally calculated IAP's for both shases are plotted in Figure 2. For the New Albany shale, the initial Fe^{3+} activity showed slight supersaturation with respect to amorphous $Fe(OH)_3$. However, with time Fe^{3+} activity approached equilibrium with $FeOHSO_4$ solid phase as pH decreased. The activities of Fe^{3+} and SO_4^{2-} for the Chattanooga shale reached equilibrium with $FeOHSO_4$ except for samples 9 and 13 which showed slight undersaturation. These results suggest that $FeOHSO_4$ mineral is verly likely controlling the activity of Fe^{3+}, in solutions below a pH of 6.00.

Acid Reactions

The results of this study demonstrate that below a pH of 6.00 the activities of Fe^{3+} and Al^{3+} are controlled by basic sulfate

solid phases. Thus, the equations describing acid production associated with pyrite oxidation below a pH of 6.00 (most acid mine drainage is well below ph 6.00) should include the following reactions:

$$Al(SO_4)(OH).5H_2O + H^+ = Al^{3+} + SO_4^{2-} + 6H_2O \quad (7)$$

$$Al^{3+} + H_2O \longrightarrow AlOH^{2+} + H \quad (8)$$

$$Al^{3+} + 2H_2O \longrightarrow Al(OH)_2^+ + 2H^+ \quad (9)$$

$$2Al^{3+} + 2H_2O \longrightarrow Al_2(OH)_2^{4+} + 2H^+ \quad (10)$$

$$FeOHSO_4 + H^+ \longrightarrow Fe^{3+} + SO_4^{2-} + H_2O \quad (11)$$

$$Fe^{3+} + H_2O \longrightarrow FeOH^{2+} + H^+ \quad (12)$$

$$Fe^{3+} + 2H_2O \longrightarrow Fe(OH)_2^+ + 2H^+ \quad (13)$$

$$Fe^{3+} + 2H_2O \longrightarrow Fe_2(OH)_2^{4+} + 2H^+ \quad (14)$$
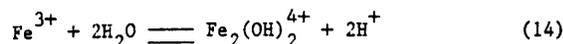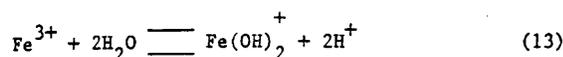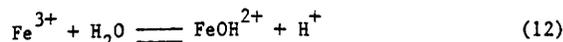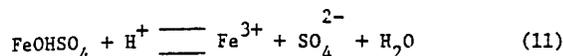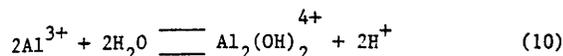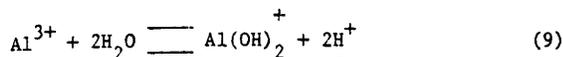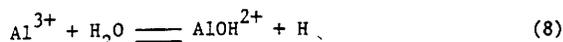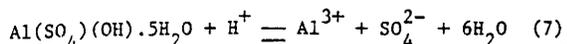
In aqueous solutions below pH 6.00, $AlOH^{2+}$, $Al(OH)_2^+$, $Al_2(OH)_2^{4+}$, $FeOH^{2+}$, $Fe(OH)_2^+$, and $Fe_2(OH)_2^{4+}$ are the predominant ionic species.

CONCLUSIONS

The results in this study suggest that below pH 6.0, depending upon SO^{2-} activity, Al^{3+} solubility was controlled by $Al(SO_4)(OH).5H_2O$ for both shales. Initially, Al^{3+} solubility for New Albany shale showed equilibrium with amorphous $Al(OH)_3$. The pH decreased with time, and Al^{3+} solubility approached equilibrium with $Al(SO_4)(OH).5H_2O$. Below pH 6.0, Fe^{3+} solubility appeared to be regulated by basic iron sulfate solid phase with the stoichiometric composition of $FeOHSO_4$. The results further suggest that the acidity in oil shale waters may be produced from the hydrolysis of Al^{3+} and Fe^{3+} in solution.

ACKNOWLEDGEMENTS

REFERENCES

1. Adams, F., and Z. Rawajfith. 1977. Basalumiminite and alunite: A possible cause of sulfate retention by acid soils. Soil Sci. Soc. Amer. J., 41:686-692.

2. Ball, T.W., E.A. Jenne and M.W. Cantrell. 1981. WATEQ3: United States Geological Survey open file report 81-1183, USGS, Menlopark, CA.

3. Filipek, L.H., D.K. Nordstrom, and W.H. Ficklin. 1987. Interaction of acid mine drainage with waters and sediments of West Squaw Creek in the West Shasta mining district, California. Environ. Sci. Technol., 21:388-396.

4. Griffin, R.A. 1980. Chemical and biological characterization of leachates from coal solid wastes. Envirn. Geol., note no. 89. Illinois Institute of Natural Resources State Geological Survey, Urbana, Illinois.

5. Lindsay, W.L. 1979. Chemical equilibria in soils. Wiley-Interscience, New York.

6. Martin, J.F. 1974. Quality of effluencts form coal refuse piles. First Symposium on Mine and Preparation Plant Refuse Disposal, Louisville, Kentucky.

7. Nordstrom, D.K. 1982. The effect of sulfate on aluminum concentrations in natural waters: Some stability relations in the system Al_2O_3-SO_3-H_2O at 298 k. Geochem. Cosmochim. Acta, 46:681-692.

8. Nordstrom, D.K. 1982. Aqueous pyrite oxidation and the consequent formation of secondary iron minerals. IN: Acid sulfate weathering: Kittrick, J.A., D.S. Fanning, and L.R. Hossner (ed.). Soil Sci. Soc. Amer.: Madison, WI, 37-56pp.

9. Nordstrom, D.K., E.A. Jenne, and J.W. Ball. 1979. Redox equilibria of iron in acid mine waters. IN: Chemical modeling in aqueous systems: Jenne, E.A. (ed.). Amer. Chem. Soc. Symp. Series, 93:857-892.

10. Rhodes, E.R., and W.L. Lindsay. 1978. Solubility of aluminium in soils of the humid tropics. J. Soil Sci., 29:324-330.

11. Runnells, D.D., and R.D. Lindberg. 1981. Hydrogeochemical exploration for uranium ore deposits: Use of the computer model WATEQFC. J. Geochem. Explor., 15:37-50.

12. Smith, R.M., W.E. Grube, T.A. Arkle, and A.A. Sobex. 1974. Mine soil potentials for soil and water analysis. EPA 670/2-74-070. U.S. Environmental Protection Agency, Washington, D.C.

13. Stumm, W. and J.J. Morgan. 1981. Aquatic chemistry. Wiley-Interscience, New York.

14. VanBreeman, N. 1973. Dissolved aluminium in acid sulfate soils and in acid mine waters. Soil Sci. Soc. Amer. Proc., 37:694-697.

15. Wahler, W.A. 1978. Pollution control guidelines for coal refuse piles and slurry ponds. U.S. Environmental Protection Agency, EPA 600/7-78-222, Cincinnati, OH.

Table 1. Activities of Al^{3+}, Fe^{3+}, Na^+, K^+, and SO_4^{2-} in distilled water extracts from pyrite containing oil shales.

SAMPLE NO.	EQUILIBRATION TIME (days)	pH	log activity				
			Al^{3+}	Fe^{3+}	Na^+	K^+	SO_4^{2-}
A. New Albany Shale (unweathered, 4.6% pyrite)							
1+	1	5.74	−6.89	−15.08	−3.11	−3.22	−1.90
2+	4	6.23	−6.72	−15.20	−3.47	−2.98	−2.48
3+	8	6.33	BD	BD	−3.14	−3.40	−1.95
4	16	7.90	BD	BD	−3.15	BD	−1.99
5	32	7.67	−13.39	−17.34	−2.71	−2.65	−2.15
6	64	7.00	−10.63	−15.80	−3.11	−3.25	−2.17
7	128	5.11	−5.68	−12.78	−2.86	−3.28	−2.26
8+	180	3.73	−14.83	−3.19	−3.33	−2.13	
B. Chattanooga Shale (weathered, 1.5% pyrite)							
9	1	4.62	−5.06	−13.45	−3.59	−3.05	−2.45
10+	4	4.66	−6.41	−14.20	−3.14	−3.37	−2.06
11+	8	3.26	−4.19	−12.35	−3.17	−2.95	−4.00
12	16	4.41	−4.93	−12.38	−3.25	−3.09	−2.26
13	32	4.02	−4.63	−11.69	−3.26	−3.06	−2.19
14	64	4.00	−4.54	−12.04	−3.28	−2.94	−2.35
15	128	3.64	−4.60	−11.30	−3.21	−2.77	−2.27
16+	180	2.44	−4.10	−10.09	−3.25	−3.09	−2.51

BD = below detection limit

+ = poor cation and anion balance
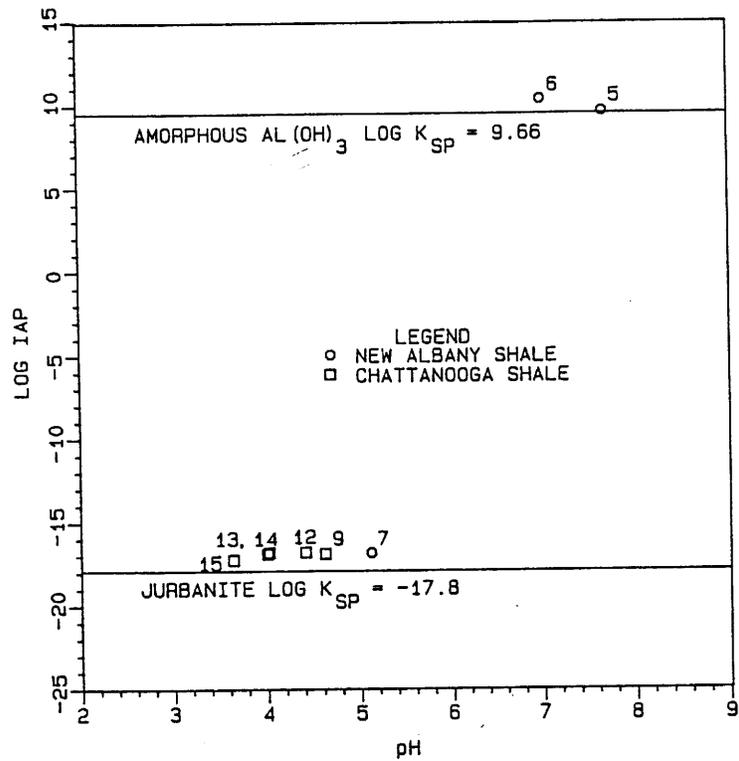
Figure 1. The solubility of Al minerals in oil shales containing pyrite.
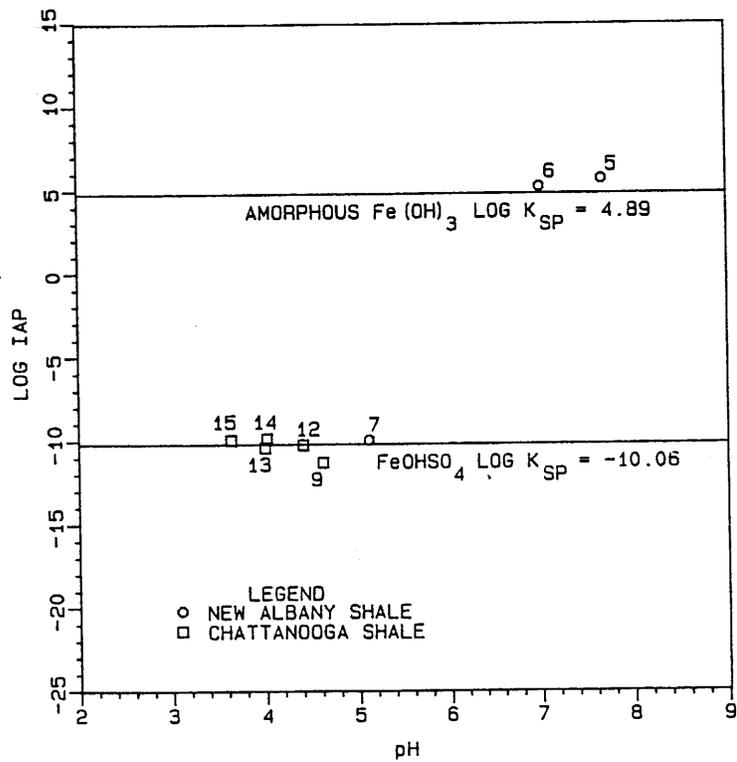
Figure 2. The solubility of Fe minerals in oil shales containing pyrite.

PROCEEDINGS

1988 EASTERN OIL SHALE SYMPOSIUM

INCLUDING TAR SANDS
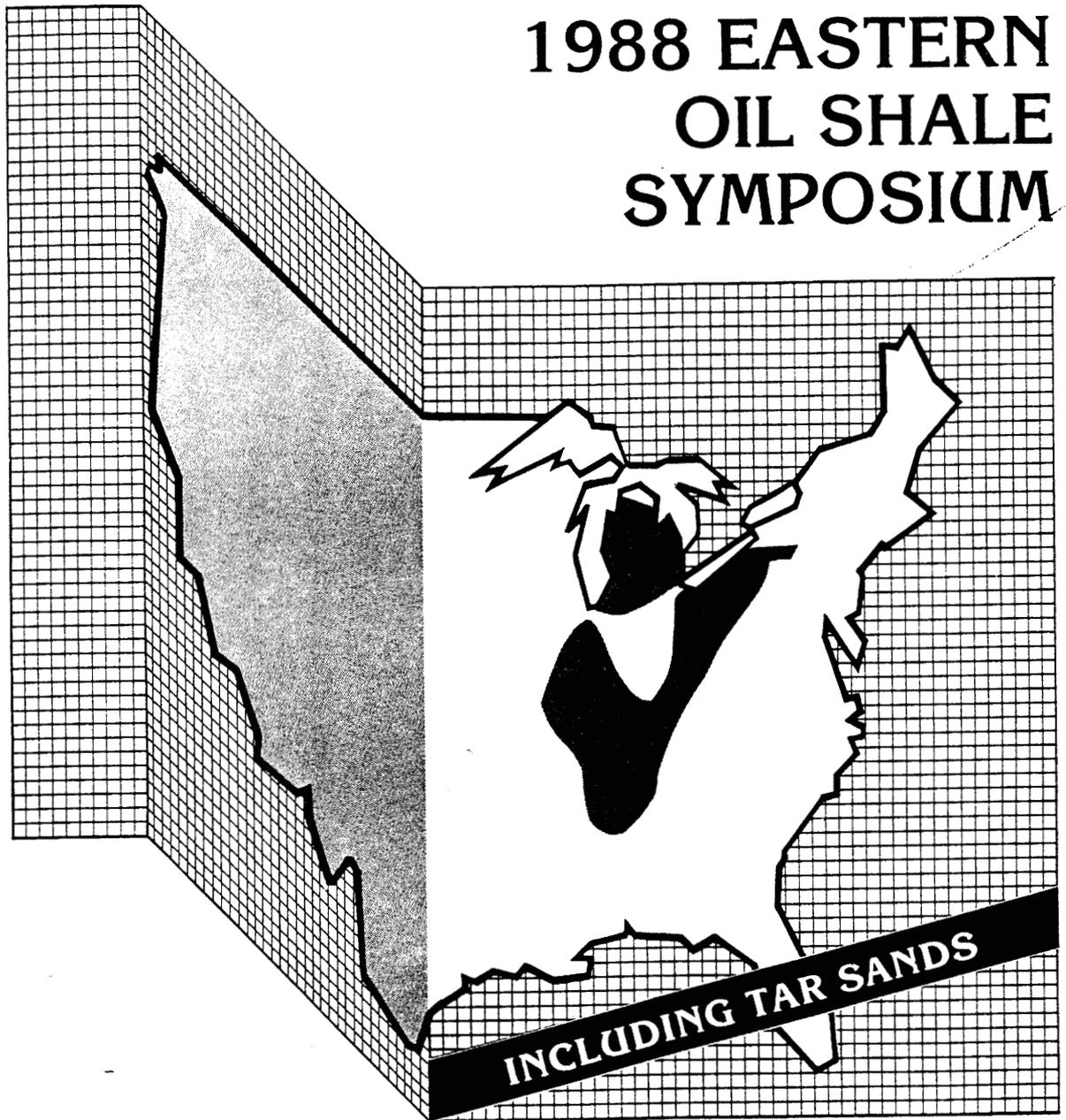
November 30 - December 2, 1988
Marriott Griffin Gate Resort
Lexington, Kentucky

Sponsored By:
UNIVERSITY OF KENTUCKY
Institute for Mining and Minerals Research
Center for Applied Energy Research

and

United States Department of Energy

and

Kentucky Energy Cabinet