Transactions of the Illinois Academy of Science
(1988), Volume 81, 1 and 2, pp. 99-112

IMPACT OF DOLOMITE AND SHALE SPOIL MATERIALS ON ILLINOIS WATER QUALITY: LABORATORY STUDIES

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ABSTRACT

The proposed construction of a Superconducting Super Collider (SSC) in north-west Illinois will generate approximately 1.5 million cubic meters of rock spoil material. Laboratory extraction experiments were conducted to investigate the potential impact of storage or land disposal of the predominantly dolomite and limestone spoil materials on water quality.

The major constituents in 39 water extracts generated by samples of likely spoil materials were Ca, Cl, K, Mg, Na, Si, and SO_4. Total organic carbon content in the extracts ranged from less than 0.05 to 9.06 mg/L. For all extracts, mean constituent concentrations were below drinking and surface effluent discharge standards. Selected spoil samples subjected to RCRA criteria were found to be nonhazardous. Solubility modeling of the water extracts predicted calcite as the prevalent mineral controlling the solubility of some constituents. Laboratory extraction and modeling studies suggest that the *in situ* leachates generated by the spoil material would be relatively innocuous, having no adverse effect on local surface and groundwater sources.

INTRODUCTION

It has been proposed that a Superconducting Super Collider (SSC) be constructed in northwestern Illinois. Construction of this underground facility will generate spoil rock material that would be stored or disposed at ground surface facilities (i.e., abandoned dolomite quarries and/or gravel pits). In order to plan for use, storage and disposal scenarios of the spoil materials that will protect water supplies, it is necessary to assess the relative solubility of any potential pollutants in the solid waste. Laboratory extraction studies were conducted to evaluate the prevalent extractable constituents in the spoil materials.

Geologic studies (Kempton et al. 1985, 1986, 1987) have indicated that the SSC facility will be housed in a tunnel constructed principally in the Galena-Platteville Dolomite Groups, located approximately 122 m (400 ft) below land surface. Approximately 1.5 million cubic meters (m^3) of spoil rock material would be excavated from the tunnel. Curran (1986) estimated the spoil would consist of by volume: 2.6% (40,404 m^3) glacial till, 0.3% (4,527 m^3) sand and gravel, 3.0% (45,110 m^3) shale, 18.9% (290,756 m^3) limestone, and 75.3% (1.1×10^6 m^3) dolomite.

Alternative uses other than long-term storage of the predominantly dolomitic spoil include concrete aggregate, fill in construction projects, and the reconstruction of the Kaneville Esker in Kane County. The shale material has been used as a liner in waste disposal pits as well as fill (Kolata, 1986). Unless markets or special uses are found, permanent disposal or long-term storage of the spoil is likely. In any event, because much of the material will be placed at land surface locations, environmental study of the spoil is warranted.

MATERIALS AND METHODS

During an investigation to describe the geology of the proposed SSC tunnel site by the Illinois State Geological Survey (Kempton et al. 1985, 1986) seventeen 4.76-cm (1.88-in) diameter cores were collected in Cook, DeKalb, Du Page, Kane and Kendall Counties. These cores were selected because they represent the stratigraphic units that would be excavated and encompass the proposed tunnel site. Thirty-nine samples were collected from these cores and subjected to laboratory extraction studies. These samples represent the seven major lithologies that would be excavated during tunnel construction. These stratigraphic units and representative lithologies include: (1) Galena Group, Wise Lake Formation, dolomite; (2) Galena Group, Dunleith Formation, dolomite; (3) Galena Group, Wise Lake Formation, limestone; (4) Maquoketa Group, dolomite; (5) Maquoketa Group, shale; (6) Silurian formations (undifferentiated) dolomite; and (7) Platteville Group, dolomite (Fig. 1).

The American Society for Testing and Materials (ASTM) water shake extraction procedure was used as a rapid means of obtaining a solution for the evaluation of the water extractable materials from a solid sample (ASTM, 1982). The U.S. EPA Toxicity Characteristic Leaching Procedure (TCLP) determined if the spoil materials would be considered hazardous under U.S. EPA extraction procedure toxicity guidelines (U.S. EPA, 1986).

A Jarell-Ash Model 975 inductively coupled argon plasma spectrometer was used to determine the concentrations in solution of Al, As, B, Ba, Be, Ca, Cd, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, P, Pb, Sb, Se, Si, Sn, V, and Zn. Chloride and sulfate were measured by a Dionex 2110i ion chromatograph. Oxidation-reduction potential (Eh), pH, and electrical conductance (EC) were measured by electrode. Total organic carbon (TOC) concentrations were ascertained using a Dohrman DC-80 carbon analyzer. Refer to Krapac et al. (1984) for a listing of detection limits.

RESULTS AND DISCUSSION

Results of the ASTM shake test indicated that all extracts were alkaline with pH values ranging from 7.60 to 10.1. Of the 27 constituents analyzed for in the extracts, only nine constituents (B, Ba, Ca, Cl, K, Mg, Na, Si, and SO_4) were at concentrations greater than analytical detection limits. The average concentrations of these analytes indicated that the trend in concentrations was $SO_4 > Mg > Ca > Na > Cl > K > Si > B > Ba$ (Table 1). However the large standard deviation of such analytes as SO_4 and Na suggest large variations in concentrations between the various samples. Evaluation of constituent concentration in extracts generated by the same solid sample lithology resulted in a general ranking of $Mg > Cl > SO_4 > Ca > Na > K > Si$. Concentrations of the remaining sixteen constituents (Al, As, Be, Cd, Co, Cr, Cu, Fe, Mn, Mo, Ni, P, Pb, Sb, Se, Sn, V, and Zn) were below detection limits in all extracts.

The extract data were grouped by the seven sample types (i.e., the seven major stratigraphic units) used to generate the extracts. Trends were apparent when the average concentrations for the various constituents were compared for the different sample types (Table 2). The general trends noted in this evaluation were: (1) Maquoketa shale extracts had greater Ca, K, Na, SO_4, and TOC concentrations and lower pH values than the other extracts; (2) Galena Group, Wise Lake limestone extracts often contained the lowest constituent concentrations; and (3) dolomite extracts from samples of the Galena Group, Dunleith and Wise Lake Formations were similar in composition.

A one-way analysis of variance (ANOVA) was performed on the extract data to ascertain if the mean-constituent concentrations were significantly different among the seven sample types at a significance level of 5% ($\alpha = 0.05$). Chloride, Mg, Si, and TOC concentrations in all of the extracts were not significantly different from each other, while Ca, K, Na, and SO_4 concentrations, and pH and EC were different in extracts generated by the various sample types. Results of the statistical evaluation suggested that *in situ* leachates generated by the various spoil materials would be significantly different from each other.

ASTM extract data were compared to drinking water and surface discharge effluent standards to evaluate the potential environmental impact of disposal of the tunnel spoil on surface and groundwater supplies. The approach used in this comparison was to average the concentrations for all 39 extracts. The rationale behind this approach was that the various spoil materials would likely be mixed at the disposal site, and the process of averaging constituent concentrations in all the extracts would best approximate leachate concentrations under these conditions. Table 3 compares the average extract constituent concentration with drinking water and surface effluent discharge water quality standard concentrations. In all cases, where standards are available, extract constituent concentrations and pH values were within the standard ranges.

Total organic carbon (TOC) analysis was used to quantify but not identify the organic components in the ASTM extracts. The TOC results suggested a slight potential for the leachates generated by the tunnel spoil materials to contribute to the organic loading of surface or groundwater sources. The range of organic carbon concentrations in the extracts was from less than detection limits (0.05 mg/L) to 9.66 mg/L, with approximately 50% of the extracts containing concentrations less than 1 mg/L. The relatively low organic carbon contents of the extracts implied that any organic loading by leachates from the spoil on surface and subsurface waters would be minor.

Individual compound identification of the organic fraction of the extracts was not performed. Organic compounds considered hazardous and/or subject to regulation are generally derived from industrial processes (i.e., insecticides and herbicides). Because the spoil material would be excavated from deeply buried stratigraphic units, the potential of the spoil to be contaminated by industrial wastes or surface runoff is minimal and compound identification was deemed unnecessary. The potential impact of the organic component of the spoil leachate on receiving surface and groundwater sources was concluded to be minimal.

Toxicity Characteristic Leaching Procedure (TCLP)

The Resource Conservation and Recovery Act (RCRA) of 1976 was enacted as a first attempt at setting guidelines for hazardous waste disposal. Of particular significance were procedures and standards to ascertain if a waste would be considered hazardous. As mandated by RCRA, there are 6 categories of hazardous wastes: (1) ignitable, (2) reactive, (3) infectious, (4) corrosive, (5) radioactive, and (6) toxic. The spoil material would not be classified as hazardous according to the criteria of the first five categories. However, the criteria establishing the toxicity of a substance are complex and involve generation of an extract. The waste can be classified as toxic if an extract obtained by the TCLP has trace metal concentrations greater than the primary drinking water standards by a factor in excess of 100, and/or the extract produces gene mutation or DNA damage in bacteria or mammalian cells.

Seven core samples, representing typical rocks from each of the major stratigraphic units which would be excavated during SSC tunnel construction, were subjected to the TCLP to evaluate if the spoil material would be considered hazardous by the toxicity criteria. The constituent concentrations that were above analytical detection limits in the TCLP extracts are given in Table 4. Based on the constituent concentrations in the extracts, the wastes would not be classified as toxic. Facilities to evaluate whether the extract would produce gene mutation were not available at the Illinois State Geological Survey. However, based on constituent concentrations in the TCLP extracts, the spoil material would not be classified as hazardous.

Equilibrium-Solubility Modeling of the ASTM Laboratory Extracts

The application of chemical equilibrium models can lead to useful insights into the geochemistry of aqueous systems, such as leachates generated by landfilled tunnel spoil materials, particularly in resolving the origins and interactions of the constituents dissolved in solution.

As a step towards understanding the extracts, chemical analyses of seventeen of the ASTM extracts were treated by the thermodynamic model WATEQ2F (Truesdell and Jones, 1974; Plummer et al., 1976; and Ball et al., 1979). This computer program calculated the ionic strength of each solution from the input chemical data. Calculated ionic strengths were used to determine single-ion activity coefficients via a Davies-extended Debye-Huckel equation that was used to convert solution concentrations to thermodynamic activities. These calculated activities were plotted on mineral stability diagrams.

The primary reason for subjecting the core samples to the short-term (48-hour) ASTM procedure was to assess water-soluble constituents in the tunnel spoil materials. A period of 48 hours may or may not be long enough for all dissolution-precipitation reactions to reach equilibrium. The lack of equilibrium conditions may, in some cases, preclude the assessment of solubility relationships. To assist in the analysis, three of the carbonate samples were extracted for 45 days to provide a limited basis for comparison (Table 5). Constituent concentrations in the 45-day extracts were higher, and pH values lower than in the 48-hour extracts.

The solution equilibria of the extracts appeared to be relatively simple. After 48 hours of contact, all of the extracts of the dominantly-carbonate samples (i.e., the dolomite and limestone facies of the Galena-Platteville and Maquoketa Groups, and the Silurian formations) were supersaturated with respect to dolomite (Fig. 2). Consequently while dolomite was present in the solid wastes, it appeared that it was not controlling the aqueous solubility of Ca^{2+}, Mg^{2+}, or the pH of the solutions. The extracts may not have reached equilibrium with respect to dolomite during the 48-hour extraction interval. The time required to establish dolomite equilibrium is unknown (Stumm and Morgan, 1981). Moreover, the conditions under which dolomite precipitates in nature are not well understood. After 45 days of contact, the three carbonate samples (SSC 2, 4, and 14) remained supersaturated with respect to dolomite.

After 48 hours of contact, all carbonate extracts were supersaturated with respect to aragonite and calcite (Fig. 2). However, after 45 days of contact, the three carbonate samples appeared to be approaching calcite equilibrium. If the three samples that were subjected to the longer equilibrium interval were fairly representative of the other spoil materials, then it would appear that the equilibrium concentrations of Ca^{2+} and CO_3^{2-} in field leachates will be eventually controlled by calcite solubility. The extracts of the Maquoketa shale appeared to be in equilibrium with aragonite after 48 hours of contact. Aragonite could have precipitated after the dissolution of carbonate phases in the solid samples.

All of the extracts were undersaturated with respect to gypsum and anhydrite (Fig. 3). The Maquoketa shale samples contained sufficient gypsum to be detected by X-ray diffractometry, but no gypsum was detected in any of the carbonate samples. The extracts of the shale had not reached equilibrium in 48 hours; gypsum was still slowly dissolving. Roy et al. (1984) found that some laboratory extracts of coal-solid wastes known to contain anhydrite required approximately 7 days for well-defined equilibria to develop. After 45 days of contact, the three carbonate extracts (SSC 2, 4, and 14) remained undersaturated with respect to both gypsum and anhydrite (Fig. 3). These results suggest that Ca concentrations and the pH of *in situ* leachates will be influenced by calcite solubility. Sulfate concentrations would increase somewhat until the leachate equilibrated with respect to gypsum if it was present in the waste materials.

As discussed earlier, carbonate-sample extracts were characterized by relatively high pH values (pH 9.2 to 10) while extracts of the Maquoketa shale were lower; pH 7.6 to 8.3. The pH of a system containing $CaCO_3$ and water in equilibrium with the atmosphere is 8.4 (Garrels and Christ, 1965). After 45 days of contact, pHs of the three carbonate-sample extracts had decreased. Two of the extracts (SSC 4 and 14) had pH values approaching the equilibrium pH of $CaCO_3$ (pH 8.4). Thus, it was concluded that the pH of *in situ* leachates may be relatively high initially, but will gradually decrease as the leachate-spoil system equilibrates with $CaCO_3$ (and possibly Mg-carbonate) phases.

CONCLUSIONS

On the basis of this study the following conclusions were made:

1. Extracts generated by the ASTM procedure contained detectable amounts of Ca, Cl, K, Mg, Na, Si, and SO_4.
2. pH values of the extracts ranged from 7.60 to 10.10.
3. For all water based extracts, mean constituent concentrations were below drinking and surface effluent discharge standards, although some individual samples exceeded those standards.
4. Total organic carbon concentrations in the water extracts ranged from less than detection limits to 9.06 mg/L, suggesting the water soluble organic component in the spoil samples was minor.
5. Although identification of individual organic compounds in the extracts was not performed, it was assumed that since the spoil material would be exhumed from deeply buried stratigraphic units, exposure to potentially hazardous organic materials is minimal and hazardous organic compounds would not be found in either laboratory extracts or *in situ* leachates.
6. Solubility modeling of the ASTM extracts suggested that shale samples would equilibrate with calcite and thus, calcium and carbonate concentrations of *in situ* leachates would be controlled by calcite solubility.
7. Long-term extraction studies indicated that leachates from the carbonate spoils would equilibrate with $CaCO_3$. The pH of *in situ* leachates may be relatively alkaline, but will gradually decrease as the leachate spoil-system equilibrates with calcite.
8. Exposure of selected core samples to the U.S. EPA toxicity characteristic leaching procedure indicated that the spoil material would be considered nonhazardous under extraction procedure toxicity guidelines.
9. Results of laboratory extraction and modeling studies demonstrated that leachates generated by the spoil material would be relatively innocuous, and would have minimal impact on local surface and groundwater sources. Disposal of the spoil material into dolomite quarries and/or gravel pits appears to be an adequate disposal and or storage plan which will not significantly alter present groundwater quality.

ACKNOWLEDGMENTS

This study was partially funded through the "Build Illinois" program by grant number 5SSC from the Illinois Department of Energy and Natural Resources administered through the University of Illinois Board of Trustees.

The authors gratefully acknowledge the contributions and helpful suggestions made by A.M. Graese, D.R. Kolata, L. Curran, and J.P. Kempton.

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Table 1. Average concentrations (mg/L) and standard deviations of extract constituents from 39 samples.

Constituent	Average[a] Concentration	Standard deviation
B	0.14	0.25
Ba	0.02	0.09
Ca	26.4	44.0
Cl	19.7	14.3
K	9.57	14.3
Mg	42.2	18.6
Na	21.2	43.9
Si	1.61	0.79
SO_4	144	234
TOC	2.05	2.99
pH	8.75	—
EC (umhos/cm at 25°C)	448	358
Eh (mV)	270	27
Alkalinity[b]	106	25.7

[a] If concentration was less than detection limit, one-half the detection limit was used in calculation of the average.

[b] As mg/L $CaCO_3$

Table 2. Summary of extract constituent concentrations as related to sample type.

Constituents	Ranking of average constituent concentration in relation to sample type
Ca	MS > MD > PD > GDD > SD > GWL > GWD
Cl	SD > GDD > PD > MD > GWD > GWL > MS
K	MS > MD > SD > PD > GWD > GDD > GWL
Mg	MD > PD > MS > GWD > SD > GDD > GWL
Na	MS > GWL > MD > GDD > GWD > SD > PD
Si	PD > GWD > SD > CDD > MD > GWL > MS
SO_4	MS >> MD > PD >> CWD > GDD > SD > GWL
TOC	MS > SD > MD > GDD > GWL > PD > CWD
pH	GWD > CDD > GWL > SD > PD > MD > MS
EC	MS >> MD > PD > SD > GWD > GDD > GWL

SD — Silurian, Dolomite
MS — Maquoketa, Shale
MD — Maquoketa, Dolomite
GWD — Galena, Wise Lake, Dolomite
GWL — Galena, Wise Lake, Limestone
GDD — Galena, Dunleith, Dolomite
PD — Platteville, Dolomite

Table 3. Comparison of average extract constituent concentration with drinking water and effluent standards.

Constituents	Average Concentration in Extracts[a,b]	Drinking Water Standards[b]	Effluent Standards for Surface Discharge[b]
B	0.14	N/S	N/S
Ba	0.02	1.0	2.0
Ca	26.4	N/S	N/S
Cl	19.7	250	N/S
K	9.57	N/S	N/S
Mg	42.2	N/S	N/S
Na	21.2	N/S	N/S
Si	1.61	N/S	N/S
SO_4	144	250	N/S
pH	8.75	5.5-9.5	6.0-9.0

[a] If concentration was less than detection limit, one-half the detection limit was used in calculation of the average.

[b] Concentrations in mg/L.

N/S — No standard.

Table 4. Constituent concentrations (mg/L) in U.S. EPA TCLP extracts.

Formation Lithology	Galena Dolomite	Maquoketa Dolomite	Dunleith Dolomite	Dunleith Dolomite	Maquoketa Shale	Wise Lake Limestone	Silurian Dolomite	Platteville Dolomite
Al	0.17	<0.09	0.13	0.12	<0.09	<0.09	1.58	0.31
Ba	0.02	<0.001	0.01	0.02	0.24	0.01	0.22	0.06
Ca	957	962	940	969	394	2165	649	1029
Fe	13.0	6.99	4.23	2.06	0.13	<0.04	7.53	0.21
K	<1.82	<1.82	<1.82	<1.82	23.7	<1.82	22.1	3.82
Mg	527	550	547	568	206	13.2	317	605
Mn	1.68	2.18	1.16	1.08	1.78	0.55	2.33	0.69
Na	<2.38	<2.38	<2.38	<2.38	1365	<2.38	17.0	<2.38
Si	0.30	0.25	0.27	0.34	1.82	0.07	2.83	0.38
Alkalinity[a]	2740	2780	2760	2640	2520	3380	920	2620
EC[b]	4600	4700	4600	4700	5400	5580	3400	5400
pH	5.36	5.36	5.36	5.45	5.47	5.92	4.55	5.51

[a] Total alkalinity as mg/L $CaCO_3$.

[b] Electrical conductivity (μmhos/cm).

Table 5. Comparison of constituent concentrations (mg/L) in 48 hour and 45 day extracts.

	Galena Dolomite SSC2		Maquoketa Dolomite SSC4		Galena Limestone SSC14	
Constituents	48 hr	45 day	48 hr	45 day	48 hr	45 day
B	<0.03	0.06	<0.03	0.05	<0.03	<0.03
Ba	<0.002	<0.002	0.004	<0.002	<0.002	<0.002
Ca	4.07	6.95	32.2	56.9	8.50	20.1
K	7.19	16.5	4.27	9.6	<2.76	3.88
Mg	35.5	97.0	75.2	160	7.11	16.1
Na	9.66	12.1	9.44	14.1	7.71	12.9
Si	1.89	1.88	0.76	1.45	0.83	1.85
SO_4	43.0	133	249	427	6.21	16.1
Alkalinity[a]	125	226	81	190	30	72
EC[b]	299	700	665	1090	120	250
pH	9.79	9.00	9.21	8.52	9.71	8.50

[a] Total alkalinity as mg/L $CaCO_3$.

[b] Electrical conductivity (μmhos/cm).

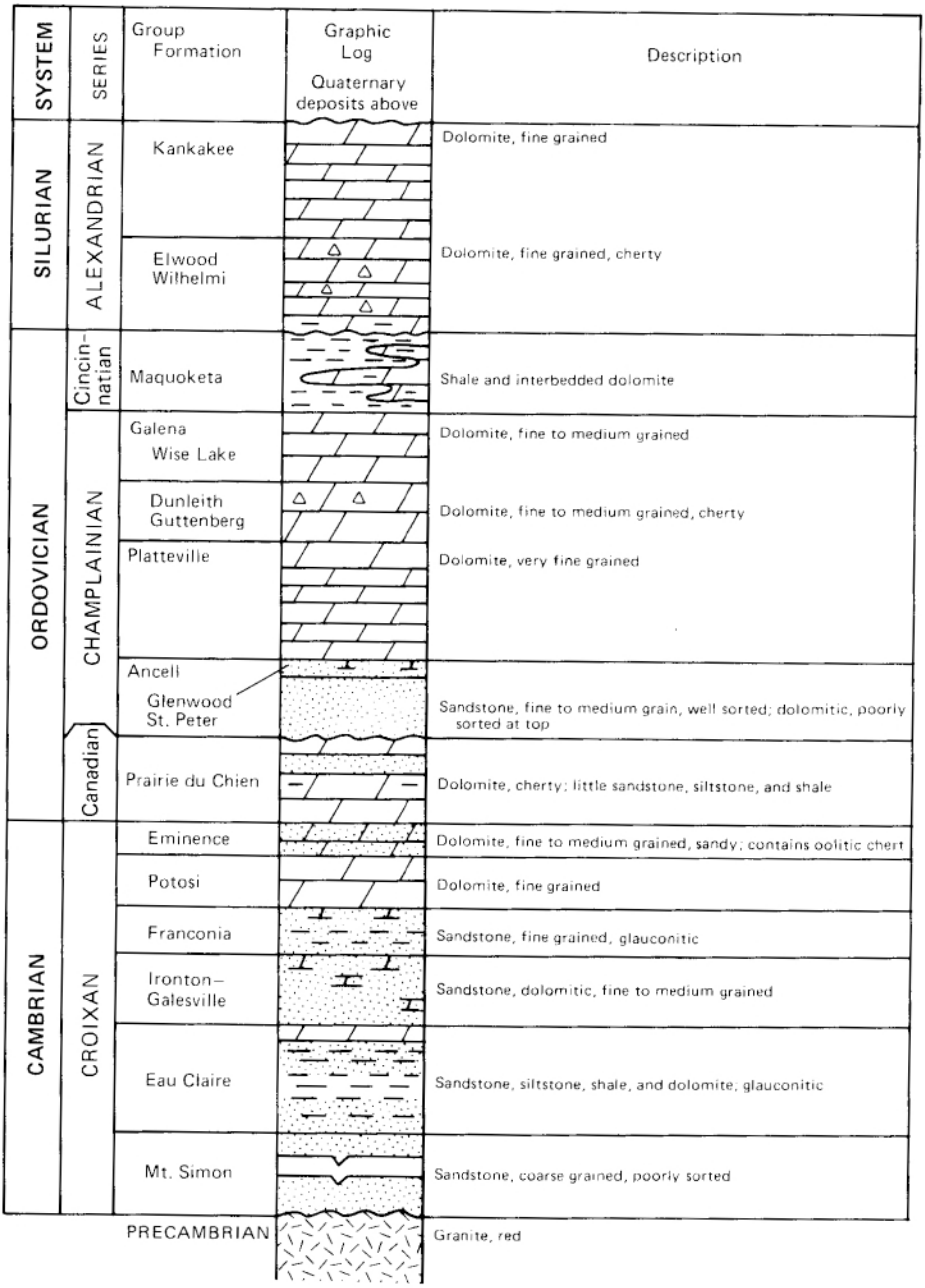

Fig. 1. Stratigraphic column of bedrock units in SSC study area (modified from Kempton et al. 1985).

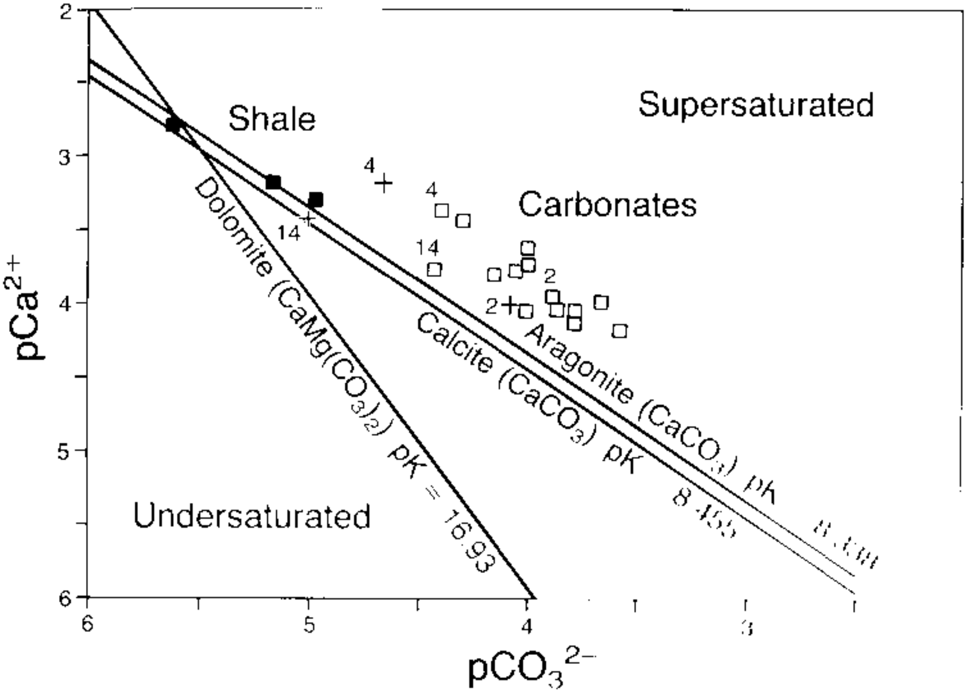

Fig. 2. Aragonite, calcite, and dolomite equilibria at 295°K, and 1 atmosphere pressure of the ASTM extracts of the core samples. The dolomite boundary was evaluated at pMg^{2+} = 3.0 M, the average Mg^{2+} content of the extracts. The squares represent the 48-hour extractions, with the solid and open squares representing the shale and carbonate samples, respectively. The crosses correlate to the long-term (45 day) extracts. The numbers (2, 4, and 14) refer to the Galena dolomite, Maquoketa dolomite, and Galena limestone samples, respectively.

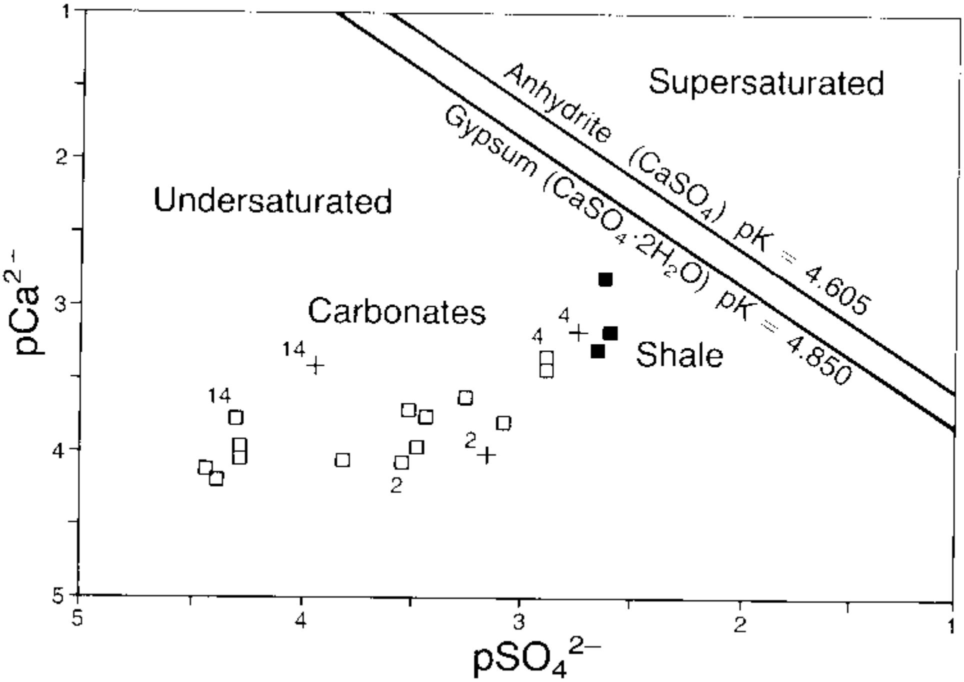

Fig. 3. Anhydrite and gypsum equilibria at 295° K, and at 1 atmosphere pressure of the ASTM extracts of the core samples. The squares represent the 48-hour extracts, with the solid and open squares representing the shale and carbonate samples, respectively. The crosses correlate to the long-term (45-day) extractions. The numbers (2, 4, and 14) refer to the Galena dolomite, Maquoketa dolomite, and Galena limestone samples, respectively.