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# **EVALUATION THROUGH LABORATORY STUDIES:**

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# IMPACT OF THE MATERIAL TO BE EXCAVATED FROM THE ILLINOIS SSC TUNNEL ON SURFACE AND GROUNDWATER SUPPLIES

Ivan G Krapac William R. Roy Robert A. Griffin Terence Beissel

**April 1987** 

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Illinois Department of Energy and Natural Resources STATE GEOLOGICAL SURVEY DIVISION

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#### Introduction

It has been proposed that materials excavated during construction of the Superconducting Super Collider (SSC) tunnel will be disposed at surface facilities (i.e., abandoned dolomite quarries and/or gravel pits). Leachates generated by water infiltrating through these materials might adversely affect the water quality of local surface and groundwater sources. To plan for disposal of the spoil material that will preserve water supplies, those chemical constituents most likely to be leached from the materials must be identified. The results of laboratory studies conducted to evaluate the prevalent extractable constituents in the spoil materials are presented here.

#### Sample Collection and Preparation

During the investigations to describe the geology of the proposed tunnel site, seventeen 3.2-cm (1.25-in) diameter cores (ISGS F1-F17) were collected from various locations encompassing the proposed tunnel area. Thirty-nine samples (SSC1-39) were collected from these cores for the laboratory extraction studies. These samples represent the seven major stratigraphic lithologies that would be excavated during tunnel construction. These stratigraphic units 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. Appendix A identifies the samples, the depth and the core number from which they were collected along with the corresponding group, formation, and rock lithology.

The collection of the samples involved dividing a section of core (approximately 20.3 cm long) in half using a rock saw. Samples of at least 500 g were required to perform the extraction studies. The length of each core section sampled varied slightly to assure that a sufficient size sample was obtained. All samples were stored in plastic bags to minimize their oxidation.

#### Extraction and Analytical Procedures

The American Society for Testing and Materials (ASTM) water shake extraction is a method to rapidly obtain a solution for evaluation of the water extractable materials from a solid sample (ASTM, 1982). The ASTM procedure was modified in two ways for use in this study. First, a smaller sample size (100 g rather than 700 g) was used. Second, the spoil material was not used in the same form in the extractions as it would be disposed. Following this ASTM recommendation would have precluded subsampling of the core. Sample reduction and division as outlined in the U.S. EPA Toxicity Characteristic Leaching Procedure (TCLP) was employed (U.S. EPA, 1986). The basic elements of this step were to crush the core samples using a large jaw crusher until 95% (by weight) of each sample passed through a 9.5-mm (3/8-in) standard sieve. The samples were then split using a riffle splitter to obtain sample sizes appropriate for the extraction procedures. From these samples, 25% slurries (solid wt/liquid vol) were prepared.

The ASTM extraction procedure involved agitating a slurry composed of  $\pm 0.01$  g of a core sample with a volume of deionized water equal in

milliliters to four times the weight in grams of the sample. The slurries were made in 500-mL wide-mouth glass bottles that were sealed with Teflonlined plastic lids and mixed at room temperature for 48 hours on a National Bureau of Standards (NBS) rotating tumbler operated at 29  $\pm$  2 rpm. The slurries were allowed to settle for 0.5 hour after mixing; oxidation-reduction potential (Eh), pH, and specific conductance (EC) were measured immediately after opening each bottle. The slurries were then decanted, and the supernate was filtered through Millipore® 0.45-µm pore size cellulose acetate membrane filters. Three subsamples of the filtrate were taken for cation, anion, and total organic carbon (TOC) analysis.

The TCLP was used to determine if the spoil materials would be considered hazardous under U.S. EPA extraction procedure toxicity guidelines (U.S. EPA, 1986). The procedure requires that either a sodium hydroxide-glacial acetic acid (pH 4.9) or a glacial acetic acid (pH 2.9) solution be used as the extraction media. Preliminary extraction studies of the spoil materials ascertained which extraction media would be used in the TCLP. All the spoil samples required the glacial acetic acid media except the Maquoketa shale samples. The procedure involved the agitation of a slurry composed of 100  $\pm$  0.01 g of spoil material with a volume of the appropriate extraction fluid equal in milliliters to 20 times the weight in grams of the sample. The slurries were made in 2-L, wide-mouth polyethylene bottles, sealed and agitated at room temperature for 18 hours on a NBS rotary tumbler operated at 29  $\pm$  2 rpm. After agitation, the slurries were treated exactly as in the ASTM procedure, except samples for cation analysis only were collected.

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. Oxidationreduction 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.

#### Results and Discussion

An overview of the data generated by the ASTM shake test indicated that the extracts were alkaline with pH values ranging from 7.60 to 10.1 (Table 1). Of the 27 constituents analyzed for in the extracts, only 9 constituents (B, Ba, Ca, Cl, K, Mg, Na, Si, and SO<sub>4</sub>) were at concentrations greater than analytical detection limits (Appendix B). The concentrations of the remaining 16 constituents (A1, As, Be, Cd, Co, Cr, Cu, Fe, Mn, Mo, Ni, P, Pb, Sb, Se, Sn, V, and Zn) were below detection limits in all of the extracts. The general ranking of constituents in terms of concentration in the extracts was Mg > Cl > SO<sub>4</sub> > Ca > Na > K > Si. The concentrations of these 7 analytes in the 39 extracts generated by the ASTM procedure are given in Table 1.

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<sub>4</sub>, and TOC concentrations and lower pH values than the other extracts; 2) Galena Wise Lake limestone extracts often contained the lowest constituent concentrations;

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Constituent	SSC-1 <sup>a</sup>	SSC-2	SSC-3	SSC-4	SSC-5	SSC-6
В	<0.03	0.04	<0.03	<0.03	<0.03	0.07
Ba	<0.002	<0.002	<0.002	0.004	<0.002	0.004
Ca	4.07	5.59	4.29	32.2	6.80	27.5
C1	17.3	16.1	13.4	66.2	30.6	28.8
K	7.19	3.86	<2.76	4,27	3.89	4.86
Ma	35.5	39.7	43.9	75.2	33.2	75.2
Na	9,66	7.78	6.58	9.44	6.01	9.20
Si	1.89	1.74	1.53	0.76	1.68	0.99
S0µ	17.4	43.0	44.4	248	7.6	245
TOCP	<0.50	1.46	<0.50	2.41	0.56	0.78
Alkalinity <sup>C</sup>	125	114	126	81	116	96
FCd	299	320	332	665	270	600
Fhe	+321	+310	+301	+294	+313	+283
nH	9.79	9.72	9.77	9.21	9,90	9,22
<u>P''</u>	5.75	5.72	5.77	<b>J</b>	5.50	<b>J</b>
Constituent	SSC-7	SSC-8	SSC-9	SSC-10	SSC-11	SSC-12
В	0.22	<0.03	0.06	0.04	<0.03	1.00
Ba	0.01	<0.002	0.008	0.003	0.008	0.58
Ca	7.08	4.46	15.6	12.5	8.82	141
C1	22.2	11.9	24.2	20.2	26.0	27.0
K	3.59	<2.76	4,10	<2.76	<2.76	58.0
Ma	28.9	31.6	45.7	41.3	30.8	49.2
Na	9.65	3.52	3.76	3.30	5.65	87.9
Si	1.82	1.91	2.14	2.00	1.69	1.19
S0 <sub>4</sub>	6.79	5.80	89.4	81.8	14.8	529
TOCD	0.78	<0.50	<0.50	<0.50	0.76	1.90
Alkalinity <sup>C</sup>	112	124	88	91	104	166
ECd	254	225	370	355	258	1280
Ehe	+283	+272	+262	+270	+279	+307
рН	9.92	9.95	9.60	9.62	9.79	7.60
Constituent	SSC-13	SSC-14	SSC-15	SSC-16	SSC-17	SSC-18
В	0.49	<0.03	<0.03	<0.03	0.04	<0.03
Ba	<0.002	<0.002	<0.002	<0.002	0.008	<0.002
Ca	6.08	8.50	5.95	7.76	12.0	7.18
C1	13.4	16.6	20.5	33.5	38.4	23.4
K	3.33	<2.76	<2.76	<2.76	9.61	<2.76
Mg	32.1	7.11	31.3	38.8	42.1	43.1
Na	4.34	7.71	10.4	7.57	8.29	10.0
Si	2.02	0.83	3.80	1.62	1.67	1.06
S04.	20.7	6.21	17.8	4.20	49.0	21.5
T0C <sup>b</sup>	<0.50	0.52	<0.50	<0.50	4.24	0.95
Alkalinitv <sup>C</sup>	115	30	107	116	115	142
ECd	232	120	246	260	410	360
Eh <sup>e</sup>	+256	+259	+253	+238	+307	+268
рH	9.82	9.71	9.93	10.1	9.41	9.53

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Table 1. Constituent concentrations (mg/L) in ASTM shake test extracts

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Constituent	SSC-19	SSC-20	SSC-21	SSC-22	SSC-23	SSC-24	SSC-25
В	<0.03	<0.03	<0.03	0.75	<0.03	<0.03	<0.03
Ba	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002
Ca	7.57	4.44	4.66	42.4	5.14	11.3	9.08
C1	26.6	22.4	14.5	2.67	10.9	40.2	30.1
К	5.58	<2.76	5.84	38.9	3.13	3.37	5.37
Mg	31.2	35.9	34.5	13.4	24.2	49.5	48.3
Na	3.25	7.08	6.80	170	13.3	5.44	9.73
Si	1.65	1.03	1.76	<0.06	1.18	0.61	0.79
S04,	4.58	4.20	5.40	397	21.3	58.5	51.8
TOCD	2.40	1.06	3.08	5.83	2.26	9.66	2.67
Alқalinity <sup>C</sup>	112	136	138	152	88	113	121
ECa	275	290	280	1090	258	430	420
Eh <sup>e</sup>	+276	+264	+268	+259	+245	+298	+236
рН	9.53	9.92	9.58	8.31	9.53	9.40	9.38

Table 1. Continued.

.

Constituent	SSC-26	SSC-27	SSC-28	SSC-29	SSC-30	SSC-31	SSC-32
В	0.08	0.57	<0.03	0.18	0.71	<0.03	0.04
Ba	0.041	0.03	0.006	0.011	0.082	<0.002	<0.002
Ca	13.3	239	10.9	26.9	77.3	7.04	55.0
C1	<3.0	<3.0	12.0	6.0	<3.0	22.5	3.0
К	14.6	47.2	4.17	13.1	44.4	4.77	3.19
Ma	17.9	89.9	58.9	41.0	30.9	41.3	87.5
Na	7.66	171	5.42	6.06	8.37	5.00	11.9
Si	2.17	0.88	1.44	1.27	1.56	2.67	0.74
S04.	20	1270	140	90	270	51	450
TOCD	16.17	2.33	<0.50	1.17	4.53	1.03	0.69
Alkalinity <sup>C</sup>	78	87	84	90	104	108	116
ECd	260	2000	480	460	690	345	840
Eh <sup>e.</sup>	+335	+273	+252	+242	+282	+245	+261
рН	9.30	7.91	9.44	9.06	8.32	9.58	8.60

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Constituent	SSC-33	SSC-34	SSC-35	SSC-36	SSC-37	SSC-38	SSC-39
В	0.05	0.07	0.06	<0.03	0.13	0.63	<0.05
Ba	0.02	0.014	<0.002	<0.002	<0.002	0.052	<0.002
Ca	29.5	27.7	11.3	7.88	60.1	56.7	5.81
C1	13.1	30	4.0	19.2	<3.0	<3.0	52
K	7.23	7.21	3.85	<2.76	3.24	36.3	5.29
Mg	70.6	62.4	49.6	49.5	26.4	20.2	39.2
Na	3.51	6.46	4.71	3.28	9.23	151	6.10
Si	1.57	1.26	1.82	1.99	3.94	1.02	3.04
S04,	260	180	104	97	220	460	7.9
TOCD	1.03	2.07	1.07	0.66	<0.50	3.63	1.83
Alқalinity <sup>C</sup>	92	80	88	103	45	113	111
ECa	640	610	440	410	510	1100	340
Ehe	+220	+244	+237	+239	+277	+269	+249
рН	9.09	9.21	9.48	9.54	8.39	8.24	9.60

<sup>a</sup> See appendix A for sample description.

<sup>b</sup> Total organic carbon.

<sup>C</sup> Total alkalinity as CaCO<sub>3</sub>.

<sup>d</sup> Electrical conductivity  $(\mu mhos/cm)$ .

<sup>e</sup> Oxidation-reduction potential (mV) corrected for standard Zobell solution.

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

Constituent	Ranking of average constituent concentration in relation to sample type
Ca	MS > MD > PD > GDD > SD > GWL > GWD
C1	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 > GDD > MD > GWL > MS
S0 <sub>4</sub>	MS >> MD > PD >> GWD > GDD > SD > GWL
τοĊ	MS > SD > MD > GDD > GWL > PD > GWD
Ha	GWD > GDD > GWL > SD > PD > MD > MS
ĒC	MS >> MD > PD > SD > GWD > GDD > GWL

GDD - Galena, Dunleith, Dolomite GWD - Galena, Wise Lake, Dolomite

GWL - Galena, Wise Lake, Limestone
MD - Maquoketa, Dolomite
MS - Maquoketa, Shale
PD - Platteville, Dolomite

SD - Silurian, Dolomite

and 3) Galena Dunleith dolomite and Galena Wise Lake dolomite extracts 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; Ca, EC, K, Na, pH and SO<sub>4</sub> concentrations 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.

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

Constituents	Average Concentration in Extracts <sup>a,b</sup>	Drinking Water Standards <sup>b</sup>	Effluent Standards for Surface Discharge <sup>D</sup>
В	0.14	N/S	N/S
Ba	0.23	1.0	2.0
Ca	26.4	N/S	N/S
C1	19.7	250	N/S
К	9.57	N/S	N/S
Mg	42.2	N/S	N/S
Na	21.8	N/S	N/S
Si	1.61	N/S	N/S
SO,	143	250	N/S
рН	8.75	5.5-9.5	6.0-9.0

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

<sup>a</sup> If concentration was less than detection limit, one-half the detection limit was used in calculation of the average.

<sup>b</sup> Concentrations in mg/L.

N/S - No standard.

The average extract concentration for each sample type (e.g., Maquoketa shale) was also compared to the drinking water and effluent standards (Appendix C). Constituent concentrations for each sample type were less than water quality standards except for sulfate concentrations in the Maquoketa shale extracts. The pH values for all individual sample type extracts, except Maquoketa shale, exceed drinking water and/or surface discharge effluent standards.

Total organic carbon (TOC) analysis was used to quantify but not identify the organic components in the ASTM extracts. The TOC results suggested there is a nominal potential for the leachates generated by the tunnel spoil materials to contribute to the organic loading of receiving 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 percent of the extracts containing concentrations less than 1 mg/L (Table 1). The relatively low carbon content of the extracts implied that the effect of leachates from the spoil on the organic content of receiving waters would be minor.

Individual compound identification of the organic fraction of the extracts was not performed. Those organic compounds considered hazardous and/or subject to regulation (Appendix D) 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, the hazardous waste criteria have been divided into six categories: 1) ignitable, 2) reactive, 3) infectious, 4) corrosive, 5) radioactive, and 6) toxic. The spoil material would not be classified as hazardous by the first five categories. However, the critieria establishing the toxicity of a substance are complex and involve the 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.

To determine if the spoil material would be considered hazardous by the toxicity criteria, seven core samples representing the major stratigraphic units that would be excavated during SSC tunnel construction were subjected to the TCLP. The inorganic constituent concentrations that were above analytical detection limits in the TCLP extracts are presented in Table 4. Based only on the inorganic constituent concentrations in the TCLP extracts, the spoil material would not be classified as hazardous.

	SSC-2	SSC-4	SSC-5	SSC-9	SSC-12	SSC-14	SSC-17	SSC-33
A1	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		7.53	0.21
К	<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 <sup>a</sup>	2740	2780	2760	2640	2520	3380	920	2620
ECp	4600	4700	4600	4700	5400	5580	3400	5400
рН	5.36	5.36	5.36	5.45	5.47	5.92	4.55	5.51

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

<sup>a</sup> Total alkalinity as CaCO<sub>3</sub>. <sup>b</sup> Electrical conductivity (μmhos/cm).

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#### 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 the tunnel spoil materials. Such modeling efforts were conducted to go beyond simply characterizing the chemical composition of the ASTM extracts by attempting to resolve the origins and interactions of the constituents dissolved in solution. The results of such modeling may form the basis for predicting the chemical composition of in situ leachates. However, the results of such modeling must be interpreted cautiously. The lack of uniform experimental conditions in ascertaining reported values for solubility constants for mineral phases can make the determination of equilibrium controls difficult.

The primary reason for subjecting the core samples to the short-term (48hour) 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.

	SSC 2 <sup>a</sup>		SSC	4 <sup>a</sup>	SSC 14 <sup>a</sup>	
Constituent	48 hr	45 day	48 hr	45 day	48 hr	45 day
В	<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
Κ	7.19	16.5	4.27	9.6	<2.76	3.88
Mq	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
S04 .	43.0	133	248	427	6.21	16.1
Alkalinity <sup>D</sup>	125	226	81	190	30	72
ECC	299	700	665	1090	120	250
рН	9.79	9.00	9.21	8.52	9.71	8.50

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

<sup>a</sup> See appendix A for sample description.

<sup>b</sup> Total alkalinity as CaCO<sub>3</sub>.

<sup>C</sup> Electrical conductivity (µmhos/cm).

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. 1). Consequently, it was not clear if dolomite was 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 of the carbonate extracts were also supersaturated with respect to aragonite and calcite (fig. 1). However, after 45 days of contact, the three carbonate samples appeared to be approaching aragonite equilibrium. If the three samples that were subjected to the longer equilibration 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 controlled by calcite-aragonite solubility. The extracts of the Maquoketa shale were in equilibrium with aragonite after 48 hours of contact.

All of the extracts were undersaturated with respect to gypsum and anhydrite (Fig. 2). 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. Therefore, 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. 2). These results suggest that Ca concentrations will not increase beyond the measured values due to control by the calcite- aragonite solubility, but that sulfate concentrations could increase somewhat until they reached the gypsum solubility control.

As discussed earlier, the carbonate sample extracts were characterized by relatively high pH values (pH 9.2 to 10). The extracts of the Maquoketa shale were lower, pH 7.6 to 8.3. The pH of a system containing  $CaCO_3$  in water in equilibrium with the atmosphere is 8.4 (Garrels and Christ, 1965). After 45 days of contact, pH of the three carbonate-sample extracts had decreased. Two of the extracts (SSC 4 and 14) had pH values approaching the equilibrium pH of  $CaCO_3$ . 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.



Figure 1. 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<sup>2+</sup> = 3.0 M, the average Mg<sup>2+</sup> 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.



Figure 2. 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. On the basis of this study the following conclusions were made:

- 1. The extracts generated by the ASTM procedure contained detectable amounts of Ca, Cl, K, Mg, Na, Si, and SO<sub>4</sub>.
- 2. The pH values of the extracts ranged from 7.60 to 10.10.
- 3. For all water-based extracts, the 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 material is minimal and hazardous organic compounds would not be found in either laboratory extracts or in situ leachates.
- Solubility modeling of the ASTM extracts demonstrated that the shale samples equilibrated with aragonite and thus, calcium and carbonate concentrations of in situ leachates would be controlled by calcitearagonite solubility.
- 7. Long-term extraction studies indicated that leachates from the carbonate spoils will equilibrate with CaCO<sub>3</sub>. Thus, the pH of in situ leachates may be relatively alkaline, but will gradually decrease as the leachate spoil-system equilibrates with aragonite or 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 the 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. The 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.

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Sample	Sample Depth	Core		· · · · ·
No.	(ft)	No.	Group/Formation	Lithology
SSC-1	361.0-361.8	F-1	Galena/Wise Lake	Dolomite
SSC-2	372.4-373.1	F-2	Galena/Wise Lake	Dolomite
SSC-3	293.0-293.9	F-3	Galena/Wise Lake	Dolomite
SSC-4	224.9-225.8	F-4	Maguoketa	Dolomite
SSC-5	409.8-410.5	F-5	Galena/Dunleith	Cherty Dolomite
SSC-6	223.9-224.7	F-6	Maguoketa	Dolomite
SSC-7	330.2-331.8	F-7	Galena/Wise Lake	Dolomite
SSC-8	240.7-241.5	F-8	Galena/Wise Lake	Dolomite
SSC-9	417.0-417.8	F-9	Galena/Dunleith	Dolomite
SSC-10	340.2-340.9	F-12	Galena/Wise Lake	Dolomite
SSC-11	357.0-357.8	F-14	Galena/Dunleith	Dolomite
SSC-12	311.3-312.0	F-15	Maquoketa	Shale
SSC-13	200.0-201.1	F-16	Galena/Wise Lake	Dolomite
SSC-14	272.6-273.6	F-16	Galena/Wise Lake	Limestone
SSC-15	309.4-310.1	F-16	Galena/Dunleith	Dolomite
SSC-16	268.6-269.4	F-17	Galena/Dunleith	Dolomite
SSC-17	100.8-101.5	F-1	Silurian	Dolomite
SSC-18	499.0-499.7	F-1	Galena/Dunleith	Dolomite
SSC-19	74.5-75.3	F-7	Silurian	Dolomite
SSC-20	366.3-367.1	F-7	Galena/Dunleith	Dolomite
SSC-21	97.8-98.6	F-10	Silurian	Dolomite
SSC-22	234.9-235.8	F-10	Maguoketa	Shale
SSC-23	289.4-299.1	F-10	Galena/Wise Lake	Limestone
SSC-24	428.2-428.9	F-12	Galena/Dunleith	Dolomite
SSC-25	362.9-363.5	F-15	Galena/Wise Lake	Dolomite
SSC-26	241.2-242.2	E-1	Maguoketa	Dolomite
SSC-27	349.9-350.8	F-2	Maguoketa	Shale
SSC-28	452.9-453.9	F-5	Platteville	Dolomite
SSC-29	91.0-92.0	F-7	Maquoketa	Dolomite
SSC-30	165.1-166.0	F-7	Maguoketa	Shale
SSC-31	470.7-471.5	F-9	Platteville	Dolomite
SSC-32	188.5-189.4	F-10	Maguoketa	Dolomite
SSC-33	334.0-334.9	F-11	Platteville	Dolomite
SSC-34	135.2-136.2	F-12	Maquoketa	Dolomite
SSC-35	466.0-466.9	F-12	Platteville	Dolomite
SSC-36	470.2-471.2	F-14	Platteville	Dolomite
SSC-37	87.3-88.3	F-16	Maquoketa	Dolomite
SSC-38	180.6-181.6	F-16	Maquoketa	Shale
SSC-39	339.5-340.4	F-17	Platteville	Dolomite

Appendix A. Description of depth, location, and geology of samples used in extraction studies

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Constituent	Detection Limit	Constituent	Detection Limit	
Al	0.07	Mn	0.01	
As	0.04	Мо	0.02	
В	0.03	Na	2.47	
Ba	0.002	Ni	0.02	
Ве	0.004	Р	0.06	
Ca	0.09	РЬ	0.02	
Cd	0.004	Sb	0.04	
Cl	3.0	Se	0.05	
Co	0.007	Si	0.06	
Cr	0.03	Sn	0.02	
Cu	0.01	S04	3.0	
Fe	0.04	тос	0.50	
К	2.76	V	0.03	
Mg	0.08	Zn	0.02	

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Appendix B. Extract constituents and their detection limits (mg/L)

								Stan Concent	dard rations
Constituent	600	GWD	GWI	Sample Type	MD	MS		Drinking Water	Surface
Ca	8.44	6.64	6.82	12.1	34.7	111	8.08	N/S	N/S
C1	26.4	18.1	13.8	20.5	19.6	6.6	26.5	250	N/S
К	<2.67	3.44	<2.67	4.45	7.21	45.0	7.01	N/S	N/S
Mg	35.6	37.7	15.7	51.5	55.1	40.7	35.9	N/S	N/S
Na	7.25	6.82	10.5	4.67	8.56	118	6.11	N/S	N/S
Si	1.60	1.71	1.01	2.09	1.59	•94	1.69	N/S	N/S
S04	26.2	34.0	13.8	110	208	585*	19.7	250	N/S
рН	9.70*	9.71*	9.61*	9.41*	8.85	7.98	9.50*	5.5-9.5	6.0-9.0

Appendix C. Comparison of individual sample type extracts with water quality standards

GDD - Galena, Dunleith, Dolomite

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GWD - Galena, Wise Lake, Dolomite

GWL - Galena, Wise Lake, Limestone

PD - Platteville, Dolomite

MD - Maquoketa, Dolomite

MS - Maquoketa, Shale

SD - Silurian, Dolomite

N/S - No standard

\* - Exceeds standards

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Constituent	Concentration (mg/L)
Arsenic (total)	0.05
Barium (total)	1.0
Cadmium`(totaĺ)	0.010
Chloride	250.
Chromium	0.05
Lead (total)	0.05
Manganese (total)	0.15
Nitrate-Nitrogen	10.
Oil (hexane-solubles or equivalent)	0.1
Phenols	0.001
Selenium (total)	0.01
Sulfates	250.
Total Dissolved Solids	500.
Chlorinated Hydrocarbon Insecticides	
Aldrin	0.001
Chlordane	0.003
DDT	0.05
Dieldrin	0.001
Endrin	0.0002
Heptachlor	0.0001
Heptachlor Epoxide	0.0001
Lindane	0.004
Methoxychlor	0.1
Toxaphene	0.005
Organophosphate Insecticides	
Parathion	0.1
Chlorophenoxy Herbicides	
2,4-Dichlorophenoxyacetic acid (or 2,4-D)	0.1
2-(2,4,5-Trichlorophenoxy)-propionic acid, (2,4,5-TP or Silvex)	0.01

## Appendix D. Illinois drinking and effluent water standards

Source: State of Illinois Rules and Regulations Title 35: Environmental Protection, Subtitle C: Water Pollution, Chapter I: Pollution Control Board, Part 302: Water Quality Standards, Subpart C: Public and Food Processing Water Supply Standards; as amended through April 1, 1984.

ILLINOIS DRINKING WATER STANDARDS

Appendix D (Cont.)

Constituent	Concentration (mg/L)
BOD5	30.
Ammonia Nitrogen (as NO	3.0
Phosphorus (as P)	1.0
рН	6.0 - 9.0
Arsenic .	0.25
Barium	2.0
Cadmium	0.15
Chromium (hexavalent)	0.1
Chromium (total)	1.0
Copper	0.5
Cyanide	0.10
Fluoride	15.0
Iron (total)	2.0
Lead	0.2
Manganese	1.0
Nickel	1.0
Oils (hexane soluble or equivalent)	15.0
Phenols	0.3
Silver	0.1
Zinc	1.0
Total Suspended Solids	15.0
Mercury	0.0005

ILLINOIS EFFLUENT STANDARDS FOR SURFACE DISCHARGES

Source: State of Illinois Rules and Regulations Title 35: Environmental Protection, Subtitle C: Water Pollution, Chapter I: Pollution Control Board, Part 304: Effluent Standards, Subpart A: General Effluent Standards; as amended through April 1, 1984.