Natural Brines of the Detroit River Group, Michigan Basin

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ABSTRACT

Natural brines which are present within the sandstones and carbonates of the Detroit River Group (Devonian) of the Michigan Basin are of great economical importance to Michigan's chemical industry. Important brines constituents such as iodine, bromine, and chlorides of potassium, calcium, magnesium, and sodium are extracted and processed to make various important chemical compounds, all of which were valued at nearly $93 million in 1971.

All available chemical analyses of natural "virgin" brines calculated on a percent by weight basis were assembled and grouped according to increasing specific gravity and increasing depth. In addition, concentrations of calcium chloride, magnesium chloride, sodium chloride, potassium chloride, bromine, and iodine were tabulated. Graphs constructed from these tables show a definite correlation between concentrations of individual brine constituents compared to depth and specific gravity.

Integration of the geological characteristics of the Detroit River Group sediments and concentration trends of various natural brine constituents enables us to delineate areas of natural brine concentrations of potential economic importance. It is vitally important that these areas of brine concentration within the Detroit River Group should not be contaminated by wastes from deep well disposal systems, destroying their future usefulness as a natural resource.

ORIGIN

Natural brines are solutions of many soluble compounds including carbonates, sulfates, bromides, iodides, and chlorides of potassium, calcium, magnesium, and sodium. Such brines are found in the subsurface, sedimentary rock formations of Michigan and because they are found in a natural state, they are known as natural brines.

There are two major theories concerning the origin of natural brines. One is that of entrapment of sea water. Under certain circumstances, porous sediments such as sand or lime muds will retain sea water within their mass, even after lithification. Another theory is that brines were formed as a result of percolating fresh water dissolving soluble beds of salt, gypsum, and carbonates. It is most likely that a combination of both processes contributed to the origin of Michigan's natural brines, except, of course, for those brines in the Precambrian areas of the Upper Peninsula which have been attributed to volcanic activity.

ECONOMICS

Michigan's natural brine is an important raw material for the State's chemical industry whose brine wells tap brine-bearing formations and pump brines of suitable chemical composition. These brines are processed yielding iodine and compounds of potassium, magnesium, bromine, and calcium. In 1971, the value of the processed natural brine amounted to over $93 million or nearly fourteen percent of Michigan's total mineral value.

Natural brines of the Detroit River Group are of particular economical importance. As illustrated in Figure 1, various chemical companies use Detroit River brines pumped from wells located in Gratiot, Lapeer, Manistee, Mason, and Midland counties.

GEOLOGY OF THE DETROIT RIVER GROUP

The Detroit River Group extends throughout the Lower Peninsula of Michigan in the subsurface and consists principally of sandstone and carbonates with anhydrite and/or salt. Detroit River rocks crop out or subcrop in the extreme northern and southeastern parts of Michigan's Lower Peninsula (Fig. 2). In the subsurface the Detroit River Group overlies the Devonian Age, Bois Blanc

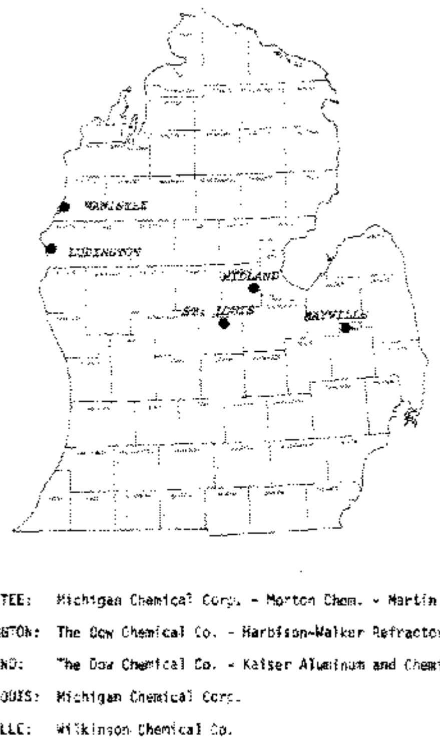

Figure 1. Locations of chemical plants producing natural brines.

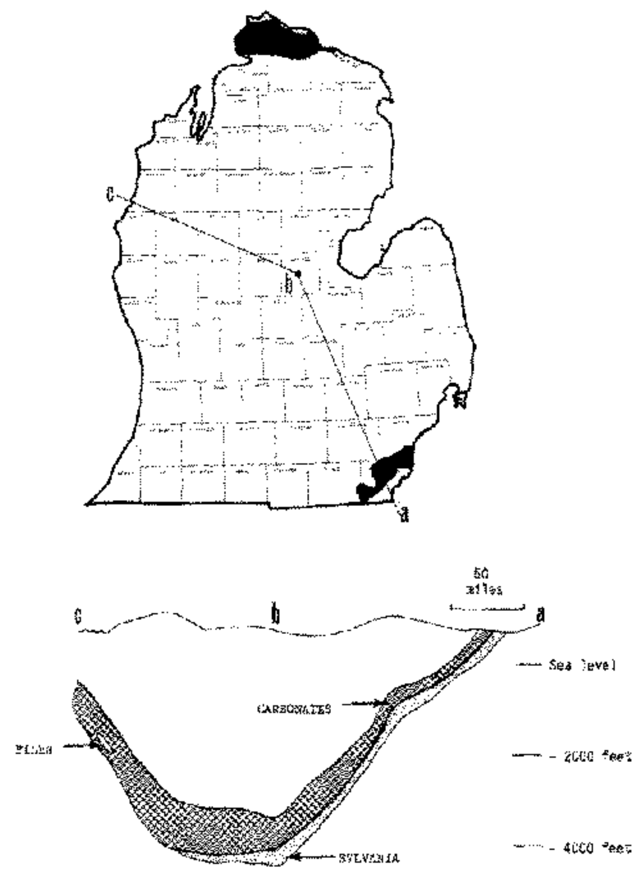

Figure 2. Map of Michigan's lower peninsula shows where rocks of the Detroit River group crop out or subcrop (shaded black) in the extreme northern and southeastern areas, the generalized cross section shows the carbonate section and filer and sylvania sandstones location within the basin.

Formation (except in western and southern Michigan where it overlies rock of Silurian Age) and is overlain by the Dundee Formation (Devonian).

The basal formation of the Detroit River Group is the Sylvania Sandstone which is present beneath southeastern, central, and west central Michigan and varies in thickness from 0–300'. The remainder of the Detroit River Group, varying in thickness from 0–1150', is generally a carbonate section consisting of the Amherstburg, Lucas, and Anderdon formations.

The Filer Sandstone has been described as either a lentil of the Amherstburg Formation (Landes, 1951) or possibly a correlative of the Sylvania Sandstone (Ells, personal communication). The Filer occurs in varying thickness within a belt in the basin which crosses from Saginaw Bay to Manistee and Mason counties adjacent to Lake Michigan. It varies in thickness from 0–100', the thickest part is located in Manistee and Mason counties.

ANALYSES OF NATURAL BRINES

All available chemical analyses of natural "virgin" brines taken from oil and gas tests and chemical wells were assembled. Since most of the available analyses were dated between 1928 and 1941 and since the geologic formations most likely were not contaminated as they are today with disposal of spent brines, these analyses reflect the chemical composition of the brines when first tapped, hence the term "virgin" brines. One limiting factor was the unavailability of confidential information directly from chemical companies, but even with the sparse data available, general assumptions can be made.

Natural brines exist throughout the Detroit River sequence, but the characteristics of brine from the basal sandstone and brines from the overlying carbonates are somewhat different and are best described separately.

NATURAL BRINES OF THE DETROIT RIVER CARBONATES

Analyses of natural brines from the Detroit River carbonates were available from various localities in Allegan, Clinton, Eaton, Huron, Isabella, Lake, Manistee, Midland, Ottawa and Saginaw counties. The following are listed in Table I for each brine sample analysis: location of well from which analysis was made, the depth below surface and converted sea level datum (SLD) from which the brine was sampled; the specific gravity and percentage of calcium chloride ($CaCl_2$), magnesium chloride ($MgCl_2$), sodium chloride (NaCl), potassium chloride (KCl), and bromine; and iodine concentration in parts per million (ppm).

TABLE I

Individual Brine Analysis of the Detroit River Carbonates

County	Location Twp.	Rge.	Sec.	Description	Depth	Depth (SLD)	SpGr.	$\%CaCl_2$	$\%MgCl_2$	%NaCl	%KCl	$\%Br_2$	PPM I_2
Allegan	4N	11W	24	NE NE SW	2263-80	−1416	1.201	7.39	2.03	14.34	.31		
	4N	16W	11	SE NW	1940	−1279	1.163	3.40	1.30	10.10	.24	.0600	
Clinton	6N	3W	19	C E 1/2 SE SE	2901-13	−2122	1.210	8.46	2.42	13.95			
	6N	3W	19	C E 1/2 SE SE	2947	−2168	1.208	8.43	2.44	14.46			
Eaton	3N	4W	6	NE SE SE	2592	−1726	1.212	7.51	2.04	17.70			
	(1)3N	6W	22	C S 1/2 SW SW	2109-15	−1213	1.190	8.60	2.57	11.66			
Huron	18N	13E	17	SW NE SE	2109-15	−2214	1.200	6.90	2.70	13.20			
Isabella	14N	3W	12	S 1/2 SE	3841	−3122	1.222	8.49	2.09	14.90	.50	.1254	
	14N	3W	12	S 1/2 SE	4200	−3481	1.296	21.23	3.60	4.58	1.57	.2919	
	14N	3W	12	S 1/2 SE	4242-49	−3523	1.282	19.90	3.40	4.93	2.34	.2770	
	14N	3W	12	S 1/2 SE	4257-73	−3538	1.293	22.05	3.78	3.39	2.64	.3037	4
	14N	3W	12	S 1/2 SE	4348	−3629	1.298	21.70	3.90	3.35	2.06	.2993	
	14N	3W	12	S 1/2 SE	4371-87	−3652	1.274	19.06	3.33	5.46	2.20	.2644	
	3W	3W	12	S 1/2 SE	4385	−3666	1.303	22.05	4.06	3.05			
	14N	3W	12	S 1/2 SE	4425-39	−3706	1.295	21.25	3.68	3.87	2.44	.2974	
	14N	3W	12	S 1/2 SE	4428-39	−3709	1.297	21.40	3.63	3.67	2.47	.3018	
	14N	3W	12	S 1/2 SE	4433-52	−3714	1.293	20.90	3.61	4.11	2.44	.2952	
	14N	3W	12	S 1/2 SE	4434	−3715	1.290	20.60	3.71	4.10	2.31	.2935	
	14N	3W	12	S 1/2 SE	4470	−3751	1.295	21.30	3.64	3.82	2.46	.2978	
	14N	3W	12	S 1/2 SE	4510	−3791	1.291	20.90	3.66	3.95	2.42	.2969	
Isabella	14N	3W	12	S 1/2 SE	4518	−3799	1.290	21.00	3.62	3.71	2.32	.2916	
	14N	3W	12	S 1/2 SE	4646	−3927	1.269	19.00	3.49	5.38	2.18	.2621	
	15N	4W	10	SE SW	3989	(−3210)	1.214	8.20	2.25	14.17	.45	.1209	
	15N	4W	10	SE SW	4472	(−3713)	1.296	21.00	3.84	3.90	2.60		
Lake	18N	11W	(25)	(C S 1/2 NE SE)	3639	(−2478)	1.206	6.10	1.70	16.70			
Manistee	21N	17W	13	NE NW	2000	−1360	1.264	13.64	8.20	5.45	.48	.2134	
	21N	17W	13	NE NW	2000	−1360	1.259	13.25	7.99	5.62	.40	.0080	
Midland	15N	1W	17	NE NE SW	3958	−3296	1.212	12.61	2.09	8.41			
	13N	1W	(21)	(C NE NE)	3890	(−3195)	1.214	8.23	1.96	15.30			
	13N	1W	(21)	(C NE NE)	4160	(−3465)	1.299	22.86	3.20	3.05			
	14N	2W	16	SW SW	4329	−3633	1.294	21.40	2.96	3.32	2.67	.2958	8
	14N	2W	16	SW SW	4590	−3894	1.296	21.06	3.55	4.06	2.36	.2982	
	15N	1E	15	NW SW SW	4000	−3350	1.245	12.86	2.85	10.99	.73		
	15N	1W	9	SW SW NE	4322-65	−3665	1.280	17 73	3.25	7.21	1.64		
Ottawa	5N	15W	34	NW SW NE	1982	−1325	1.194	5.91	1.55	11.50			
Saginaw	12N	4E	14	SW NE	3520	−2921	1.252	14.56	3.38	9.70		.1980	22
	12N	4E	14	SW NE	3560	−2961	1.287	19.46	4.20	4.99	2.89	.2835	26
	12N	4E	14	SW NE	3649	−3050	1.296	20.36	4.04	4.34	2.70	.3140	40
	12N	6E	32	NE SE SE	3470	−2838	1.287	19.00	3.80	4.40	2.65	.2735	
	13N	3E	15	SW NE	3820	−3147	1.262	16.47	4.04	4.08			

(1) Brine well of Eaton County Road Commission

Analyses were grouped by specific gravity and listed in ascending order (Table II). Where two or more analyses (the number of which is denoted under column marked "# Anal.") fell in a particular specific gravity range, the percent values for each chemical constituent were averaged. For instance in Table II, the specific gravity denoted as 1.210 includes all those analyses (in this case four analyses) having specific gravities from 1.208 through 1.212. The individual constituent values were averaged with the following results: 9.25% $CaCl_2$; 2.25% $MgCl_2$; 13.6% NaCl. In some cases, particular constituents were not determined. Such is the case for the 1.300 specific gravity class under KCl. Here, 2.13-4 denotes that the average % KCl is 2.13, but only 4 of the total of 5 analyses were tested for % KCl.

From the information listed in Table II, a series of graphs were constructed as shown in Figures 3 and 4. With increasing specific gravity, there is a general increase in concentration of constituents, calcium chloride having the most prominent increase. Sodium chloride, however, increased in concentration until brines of specific gravity of 1.210 or greater were reached, then sodium chloride concentration decreased rapidly.

Many analyses are available from Michigan Basin formations other than those of the Detroit River Group. These analyses together with the analyses herein were treated using the same technique employed above, and the resulting values for each constituent were plotted on the corresponding graph, thus giving average curves for all brines. These average curves for all brines (narrow lines)

TABLE II

Grouped Brine Analyses of the Detroit River Carbonates Percent Concentration on a Specific Gravity Basis

# Anal.	SpGr	% $CaCl_2$	% $MgCl_2$	% NaCl	% KCl	% Total* Chlorides	Br_2	PPM I_2
1	1.165	3.40	1.30	10.10	.24	14.80	.0600	
1	1.195	5.91	1.55	11.50		18.96		
2	1.200	7.14	2.36	13.77	.31–1	23.27		
1	1.205	6.10	1.70	16.70		24.50		
4	1.210	9.25	2.25	13.63		25.13		
1	1.215	8.23	1.96	15.30		25.49		
1	1.220	8.49	2.09	14.90	.50	25.48	.1254	
1	1.225	8.20	2.25	14.17	.45	24.62	.1209	
1	1.245	12.86	2.85	10.99	.73	26.70		
1	1.250	14.56	3.38	9.70		27.64	.1980	22
2	1.260	14.86	6.01	4.85	.40–1	25.72	.0080–1	
1	1.265	13.64	8.20	5.46	.48	27.29	.2134	
1	1.270	19.00	3.49	5.38	2.18	27.87	.2621	
1	1.275	19.06	3.33	5.46	2.20	27.85	.2644	
2	1.280	18.81	3.32	6.07	1.99	28.20	.2770–1	
4	1.290	20.49	3.80	4.19	2.48	28.48	.2914	26–1
7	1,285	21.20	3.64	3.81	2.41	28.65	.3011–6	
5	1.300	21.62	3.49	3.75	2.13–4	28.96	.2970–4	
1	1.305	22.05	4.06	3.05		29.16		

* percent KCl not included

appear with the Detroit River brine constituent curves (wide lines) as a comparison. In some areas the two curves coincide and appear as one line.

In Table III, analyses are grouped according to increasing depths (SLD). Trends similar to those shown on the specific gravity plots are evident on the depth plots (Fig-

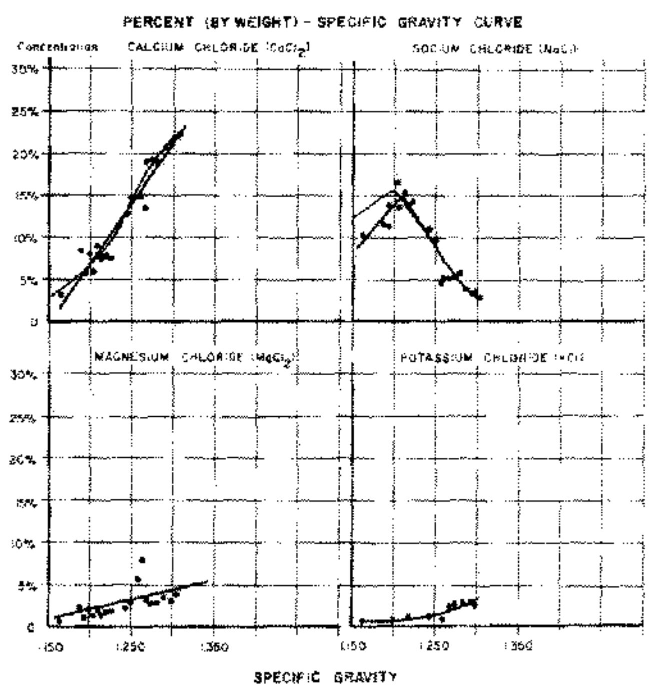

Figure 3. Detroit River carbonates, specific gravity curves.

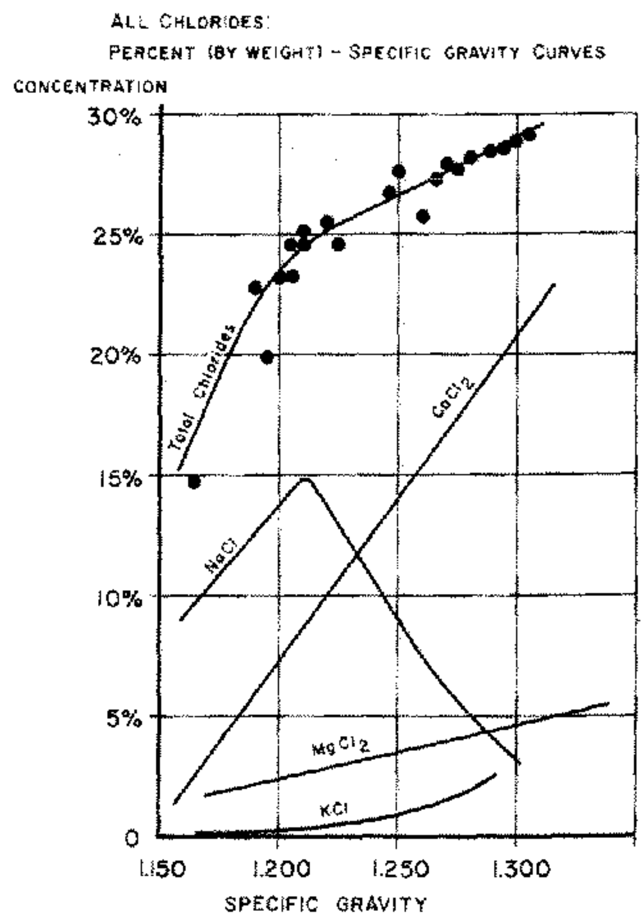

Figure 4. Detroit River carbonates, specific gravity curves.

TABLE III

Grouped Brine Analyses of the Detroit River Carbonates Percent Concentration on Depth Basis

# Anal.	Depth	SpGr	% $CaCl_2$	% $MgCl_2$	% NaCl	% KCl	% Total* Chlorides	% Br_2	PPM I_2
1	−1300	1.163	3.40	1.30	10.10	.24	14.80	.0600	
1	−1400	1.201	7.39	2.03	14.34	.31	23.76		
1	−1700	1.212	7.51	2.04	17.70		27.25		
1	−2100	1.210	8.46	2.42	13.95		24.83		
2	−2200	1.204	7.66	2.57	13.82		24.05		
1	−2500	1.206	6.10	1.70	16.70		24.50		
1	−2800	1.287	19.00	3.80	4.40	2.65	28.48	.2736	
1	−2900	1.252	14.56	3.38	9.70		27.64	.1980	22
2	−3000	1.291	19.91	4.12	4.66	2.79	28.69	.2987	33
2	−3100	1.242	12.48	3.06	9.49	.50−1	25.03	.1254−1	
2	−3200	1.214	8.21	2.11	14.73	.45−1	24.16	.1209−1	
1	−3300	1.212	12.61	2.09	8.41		23.11		
1	−3400	1.245	12.86	2.85	10.99	.73	27.70		
4	−3500	1.292	21.51	3.49	4.02	2.40	29.02	.2909−3	
2	−3600	1.296	21.55	3.49	3.33	2.36	28.37	.2975	8−1
8	−3700	1.291	20.50	3.64	4.42−7	2.30−7	28.56	.3505−5	
3	−3800	1.265	21.07	3.64	3.82	2.40	28.53	.2621	
2	−3900	1.284	20.03	3.52	4.72	2.27	28.27	.2621	

* percent KCl not included

ures 5 and 6). Calcium chloride exhibits a prominent increase in concentration with increasing depth. Sodium chloride increases until an approximate depth of −2000' SLD where its concentration decreases.

Figure 7 shows a specific gravity curve and a calcium chloride concentration curve as related to depth (SLD). It has been estimated that brines of commercial quality should have a calcium chloride concentration of approximately 12%. The 12% calcium chloride concentration is not known to be the only factor that chemical companies consider; it is merely "a pick" by the authors as the most probable lower limit to be economical. The depth (SLD) at which we will most likely find a commercial natural brine within the Detroit River carbonates can be determined. By locating the 12% calcium chloride value on the graph, we note that this will most likely occur at a depth of −2900' (SLD), and at this depth the specific gravity will most likely be 1.235.

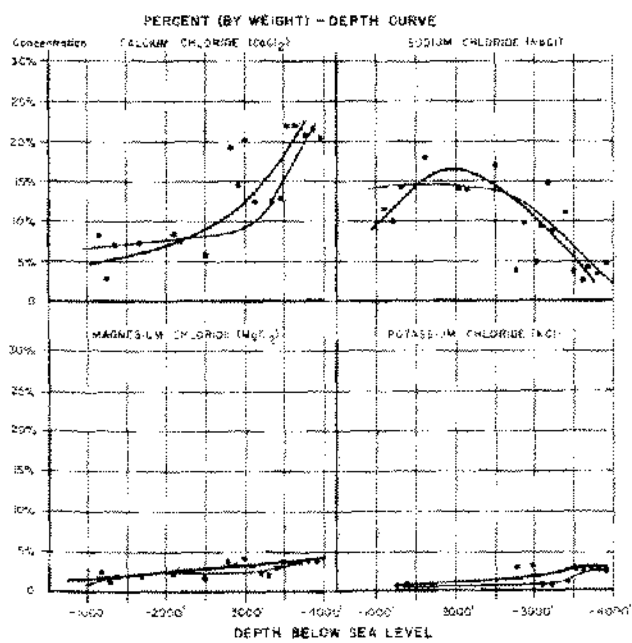

Figure 5. Detroit River carbonates, depth curves.

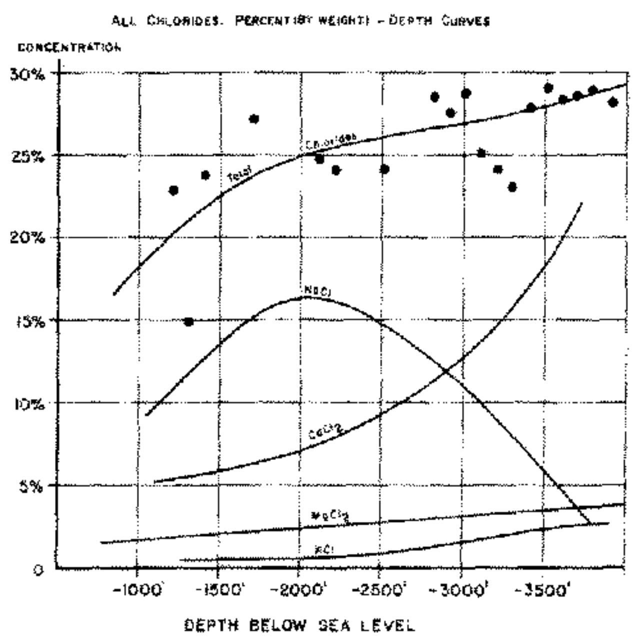

Figure 6. Detroit River carbonates, depth curves.

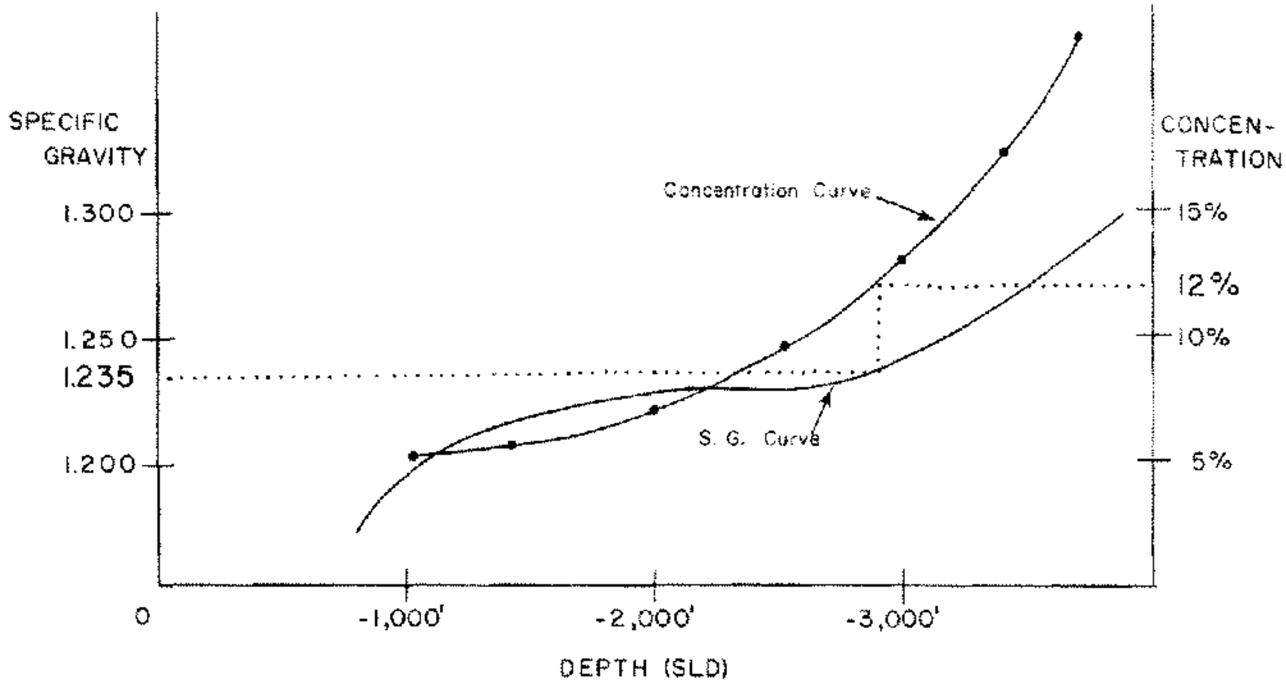

Figure 7. Calcium chloride and specific gravity vs. depth curves.

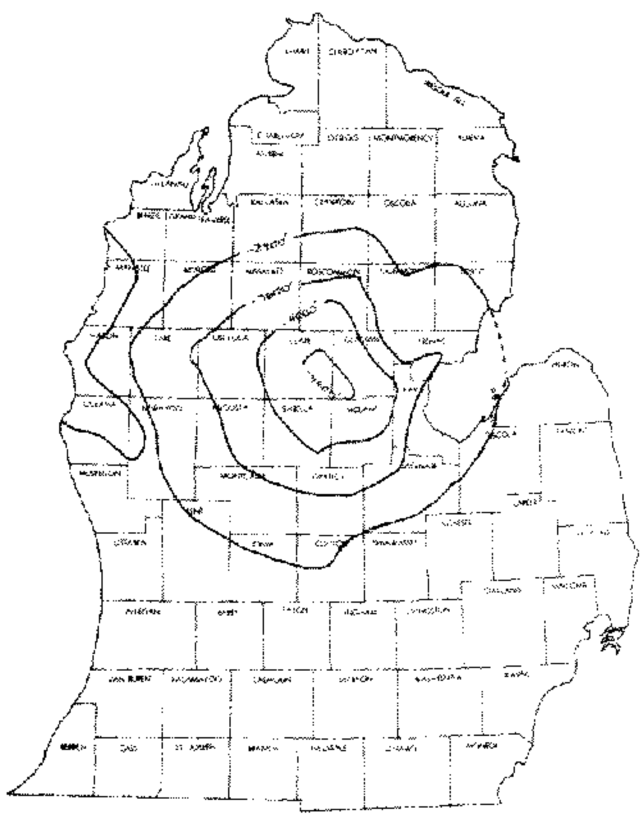

Figure 8. Detroit River Group, carbonate brines areas and depth of economic potential.

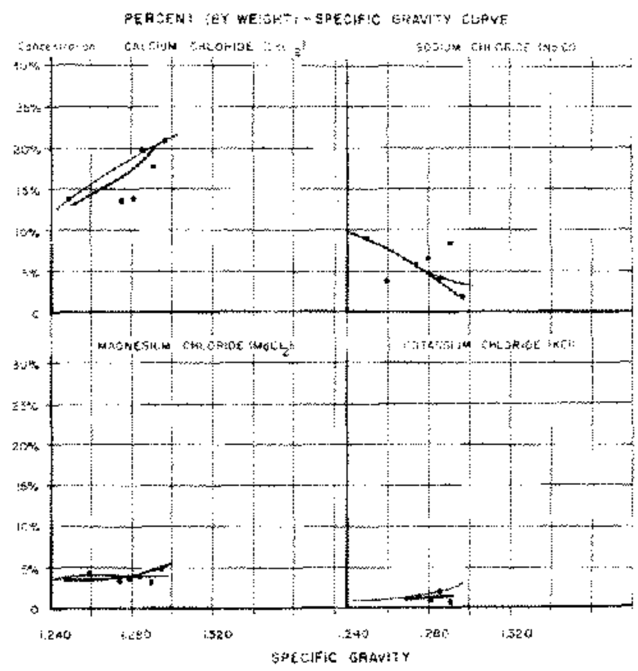

Figure 9. Sylvania sandstone, specific gravity curves.

Figure 8 illustrates the area of Michigan where the Detroit River carbonates are at a depth of -2900' (SLD) and greater. Thus, within this area, we would expect to find commercial brines within the Detroit River carbonates at -2900' (SLD) or greater. Economic brines depicted

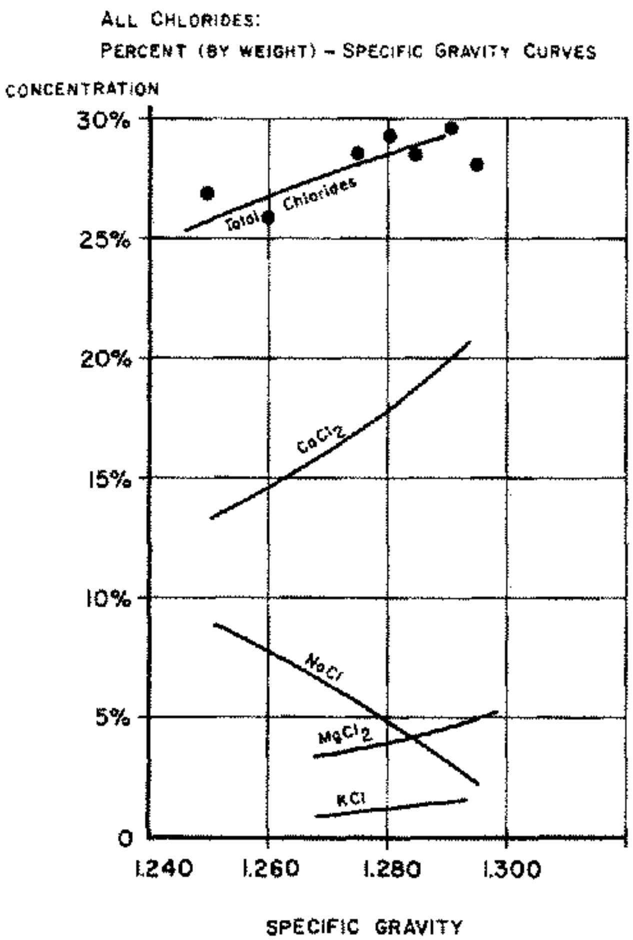

Figure 10. Sylvania sandstone, specific gravity curves.

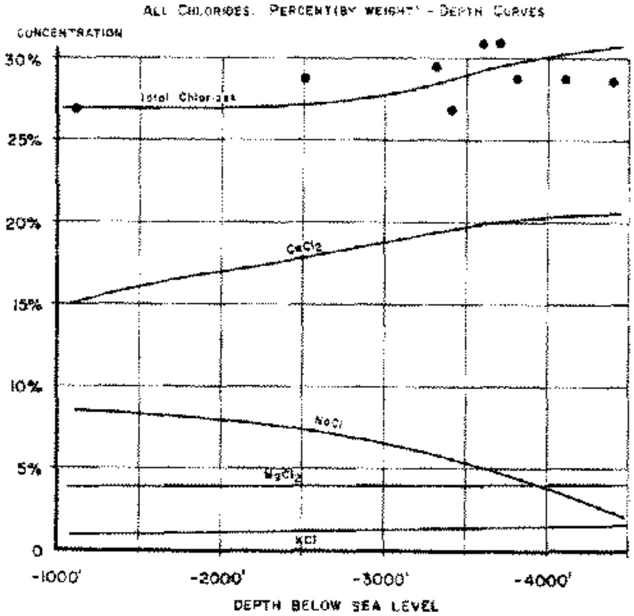

Figure 11. Sylvania sandstone, depth curve.

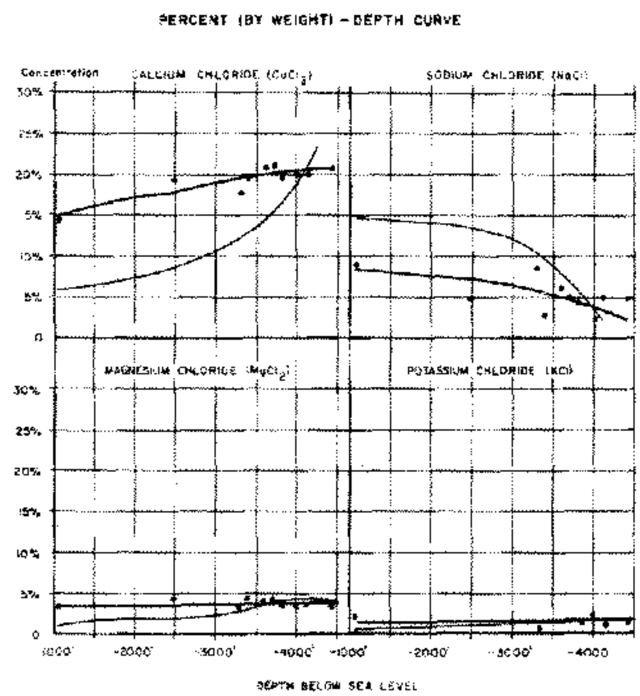

Figure 12. Sylvania sandstone, depth curves.

in the west-central area can be found at shallower depths, but this is principally due to the influence of high-quality brines within the Filer Sandstone.

Since commercial brines may exist within the limits specified, it is therefore recommended that disposal wells within this commercial area not be allowed. Injection of commercial caustic wastes or spent brines would, we feel, "pollute" available commercial brines in the area. Natural brine is an important resource and should be protected from contamination.

NATURAL BRINES OF THE SYLVANIA SANDSTONE

Analyses of natural brines from the Sylvania Sandstone were available from various localities in Bay, Gratiot, Isabella, Midland, Oakland, and Saginaw counties as listed in Table IV. As can be seen in Tables V and VI, all analyses have been grouped and statistically handled the same as the carbonate brines described in the previous section.

The series of graphs in Figures 9 through 12 were constructed from Tables V and VI. Generally speaking, concentrations of each individual chloride (except sodium chloride) are higher than in the carbonate brines, and the concentrations, although increasing remain more constant with increased depth than those in the carbonate brines.

TABLE IV

Individual Brine Analyses of the Sylvania Sandstone

County	Location Twp.	Rge.	Sec	Description	Depth	Depth (SLD)	SpGr.	%$CaCl_2$	%$MgCl_2$	%NaCl	%KCl	%Br_2	PPM I_2
Bay	14N	4E	2	C S½ SE SE	3962	–3363	1.294	21.10	4.66	2.20			
	14N	4E	2	C S½ SE SE	3967-96	–3364	1.258	18.20	4.14	3.60			
	14N	4E	2	C S½ SE SE	4177	–3578	1.288	20.70	4.19	6.10			
	14N	4E	2	C S½ SE SE	4304-09	–3705	1.283	20.30	4.06	5.50			
	14N	4E	2	C S½ SE SE	4304-35	–3705		21.80	3.96	6.20			
	14N	4E	2	C S½ SE SE	4360	–3761	1.286	20.30	3.99	4.80			
Gratiot	12N	3W	24	SE SW NW	4553	–3807	1.276	18.98	3.30	6.16	1.35	.2320	
Isabella	14N	3W	12	S½ SE	4808-21	–4089	1.282	20.10	3.64	5.00	1.09	.2540	
Lapeer	10N	10E	21	C W½ SW NW	3315	–2514	1.287	19.40	4.48	4.80	1.72		
Midland	14N	2W	16	SW SW	4697	–4001	1.285	20.00	3.50	2.41	2.11	.2751	20
	15N	1W	9	SW SW NE	5065-69	–4408	1.283	20.60	3.46	4.62	1.32		
Oakland	5N	11E	36	NE SE SW	2070-2200	–1101	1.250	14.39	3.60	8.98			
Saginaw	9N	1E	35	S½ N½ NW	4023-25	–3340	1.280	17.85	3.36	8.43	.57	.2668	

TABLE V

Grouped Brine Analyses of the Sylvania Sandstone
Percent Concentration on a Specific Gravity Basis

# Anal.	SpGr	% $CaCl_2$	% $MgCl_2$	% NaCl	% KCl	% Total* Chlorides	% Br_2	PPM I_2
1	1.250	14.39	3.60	8.98		26.97		
1	1.260	18.20	4.14	3.60		25.94		
1	1.275	18.98	3.30	6.16	1.35	28.44	.2320	
2	1.280	18.97	3.50	6.76	.83	29.23	.2589	
5	1.285	20.12	3.90	4.43	1.72	28.45	.2571-1	20-1
1	1.290	17.85	3.36	8.43	.57	29.64	.2668	
1	1.295	21.10	4.66	2.20		27.96		

* percent KCl not included

TABLE VI

Grouped Brine Analyses of the Sylvania Sandstone
Percent Concentration on Depth Basis

# Anal.	Depth	SpGr	% $CaCl_2$	% $MgCl_2$	% NaCl	% KCl	% Total* Chlorides	% Br_2	PPM I_2
1	−1100	1.250	14.39	3.60	8.98		26.97		
1	−2500	1.287	19.40	4.48	4.80	1.72	28.68		
1	−3300	1.280	17.85	3.36	8.43	.57	29.64	.2668	
2	−3400	1.276	19.65	4.40	2.90		26.95		
1	−3600	1.288	20.70	4.19	6.10		30.99		
2	−3700	1.283−1	21.05	4.01	5.85		30.91		
2	−3800	1.271	19.64	3.64	5.48	1.35−1	28.76	.2320−1	
1	−4000	1.285	20.00	3.50	2.41	2.11	25.91	.2751	20
1	−4100	1.282	20.10	3.64	5.00	1.09	28.74	.2540	
1	−4400	1.283	20.60	3.46	4.62	1.32	28.68		

* percent KCl not included

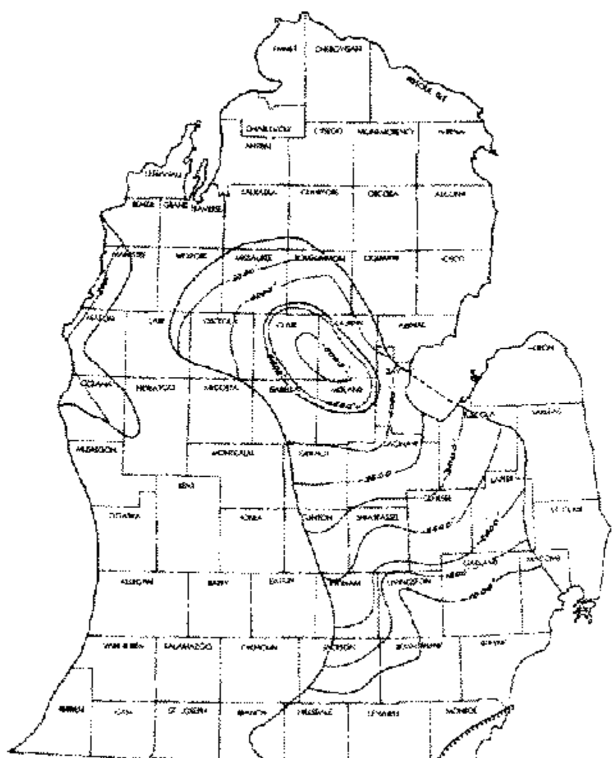

Figure 13. Detroit River group–Sylvania sandstone brines area and depth of economic potential.

The specific gravity and calcium chloride concentration are high even at a shallow depth of −1100′ SLD. It would be safe to assume that one could find a potentially economical brine within the Sylvania at a depth of −1100′ SLD or deeper; Figure 13 illustrates this area. The Sylvania Sandstone is, in fact, the most important source in Michigan for economic brines. And again, we feel that disposal within this area should not be allowed.

POINTS TO PONDER

Our charts, figures, and tables illustrate that variations in chloride concentrations and specific gravity with depth of our brines are relatively predictable and have economic significance. But, as always, new questions and challenges arise; the following are some questions pertaining to the Michigan Basin's natural brines that should be pondered.

1. What is the economic potential of all natural brines within the various rock formations of the Michigan Basin?
2. Should criteria be established to allow or forbid disposal of wastes within delineated areas of economic brine potential?
3. What is the significance of the variance in brine constituent concentration at depth?
4. What is the significance of the variance in brine constituents as related to the character of rock formation?
5. Is there a relation to the variance in brine constituents and the formation of salt, gypsum, or anhydrite?
6. What connection, if any, do the brine constituents play in the dolomitization process?

REFERENCES

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