

6-1-67

MICHIGAN WATER RESOURCES COMMISSION

Report of Industrial Survey

Michigan Chemical Company
St. Louis, Michigan

August 28 - September 1, 1967

During the week of August 28, 1967 a 48-hour wastewater survey was conducted at Michigan Chemical Company in St. Louis, Michigan. The purpose of this investigation was to determine the quality and quantity of wastes being discharged by this company to the waters of the state. Further, it was part of a comprehensive survey of the Pine River.

Production

This company produces bromine, calcium chloride, magnesium carbonate, sodium chloride and other products which were unrevealed to the survey team. The plant operates 24 hours per day, seven days per week and has approximately 385 employees. Production was normal for the duration of the survey.

Plant Processes and Sources of Waste

Figure 1 is a schematic diagram of the steps in the production of bromine, calcium chloride and magnesium carbonate at Michigan Chemical Company. Raw brine is pumped from the Sylvania and Dundee formations. After the reaction step the material consists primarily of CaCl_2 , NaCl and $\text{Mg}(\text{OH})_2$. Since $\text{Mg}(\text{OH})_2$ is highly insoluble in comparison to the two chloride compounds it is essentially purified by pumping it through the three successive thickeners. The MgCO_3 is produced by the addition of CO_2 to the purified $\text{Mg}(\text{OH})_2$.

The supernatant from the first thickener contains relatively high concentrations of CaCl_2 and NaCl . This solution is pumped to the anhydrous plant where the two chloride compounds are separated and the sodium chloride is discharged with the wastewater effluent.

Survey Procedure and Results

There are approximately 20 separate wastewater discharges from Michigan Chemical Company to the Pine River. Ten weirs were constructed by the survey team (Fig. 2, also Fig. 3-12 of file copy). Some of these weirs intercepted the discharge from two or more sources. Table 1 provides an explanation of the size and type of weir construction and information concerning possible chemical constituents, flow estimates and sources of waste of the various effluents. Most of this information was given to the survey team by company personnel.

Stevens Type F water level recorders and automatic samplers were installed at the weir sites. The recorders maintained a continuous account of the head of water being discharged over each weir. The samplers took samples proportional to the flow at 15-minute intervals throughout the duration of the survey. These samples were deposited in clean glass containers to make up 24-hour composite samples.

Table I. Information pertaining to wastewater discharge stations, Michigan Chemical Company, St. Louis, Michigan, MWRC survey of week of August 28, 1967.

<u>Outlet No.</u>	<u>Method of measurement</u>	<u>Process origin and/or possible waste constituent</u>
1	90° V-notch weir	Pilot plant effluent (HBr scrubber water, HCl, H ₂ SO ₄ , waste alum, acetic acid washes, brominated phenols)
2	30-inch rectangular weir	Rare-earth plant effluent (CuSO ₄ , oxalic acid, EDTA, NaOH, H ₂ SO ₄ , HCl, CaCl ₂ , SO ₂ fumes from scrubber, acetic acid)
3	90° V-notch weir	Scrubber and condenser water, HCl fumes
4	None (submerged outlet)	Fe(OH) ₃
5	Estimated by company from pump data	Primarily cooling water from Intake #1 HCl from salt plant
6	24-inch rectangular weir	NH ₃ , tribromopropane, dibromopropane dibromochloropropane, H ₂ SO ₄ , benzene
7	18-inch rectangular weir	Trichlorobromomethane, NaCl, HBr, NaOH, brominated organics
8	None	Tail brine from #1 thickener
9	36-inch rectangular weir	CO ₂ scrubber water, excess debrominated brine, MgCO ₃ filtrate
10	90° V-notch weir	Floor washings from slaker plant; leakage from packing gland in slaker plant
11	48-inch rectangular weir	Overflow from #2 thickener
12	None (intermittant discharge)	Wastewater resulting from softening process and from result of breakdown of #1 thickener
13	72-inch rectangular weir	CaCl ₂ plant cooling water, condensate off brine and NaCl from concentration step of brine
<u>Intake No.</u>		
1	Estimated by company from pump data	Intake water from river
2	Estimated by company from pump data	Intake water from river

There are two river-water intakes at Michigan Chemical Company. Since these intakes are pumped they are essentially constant in flow. The discharge at outlet number 5 is nearly constant in flow volume also since it consists primarily of cooling water. Siphon samplers (Figures 13; 14; 15 of file copy) were installed at these three locations and 24-hour composite samples were collected.

Composite samples from outlets number 4 and 12 were collected by hand sampling techniques. A weir was constructed at outlet number 8 (Figure 8, file copy), however, a flow was observed at this site only once throughout the 48-hours of the survey. This was at approximately 9:00 p.m. on August 31, and a grab sample was collected.

Grab samples for phenol, bacteriological and dissolved oxygen analyses were collected at periodic intervals throughout the duration of the survey.

Table 2. Wastewater flows, Michigan Chemical Company

Outlet No.	Survey 1			Survey 2		
	From	To	Avg. flow mgd	From	To	Avg. flow mgd
1	8:30A, 8/30/67	8:30A, 8/31/67	0.031	8:30A, 8/31/67	8:30A, 9/1/67	0.032
2	8:45A, 8/30/67	8:45A, 8/31/67	0.354	8:45A, 8/31/67	8:45A, 9/1/67	0.272
3	9:00A, 8/30/67	9:00A, 8/31/67	0.078	9:00A, 8/31/67	9:00A, 9/1/67	0.067
4			-----			-----
5	10:30A, 8/30/67	10:30A, 8/31/67	4.32	10:30A, 8/31/67	10:30A, 9/1/67	4.32
6	9:30A, 8/30/67	9:30A, 8/31/67	0.460	9:30A, 8/31/67	9:30A, 9/1/67	0.497
7	9:45A, 8/30/67	9:45A, 8/31/67	0.301	9:45A, 8/31/67	9:45A, 9/1/67	0.246
8			-----			-----
9	10:00A, 8/30/67	10:00A, 8/31/67	0.200	10:00A, 8/31/67	10:00A, 9/1/67	0.172
10	10:00A, 8/30/67	10:00A, 8/31/67	0.021	10:00A, 8/31/67	10:00A, 9/1/67	0.027
11	9:45A, 8/30/67	9:45A, 8/31/67	0.86	9:45A, 8/31/67	9:30A, 9/1/67	0.95
12			-----			-----
13	9:30A, 8/30/67	9:30A, 8/31/67	3.38	9:30A, 8/31/67	9:30A, 9/1/67	3.41
Intake No.			<u>10.005</u>			<u>9.993</u>
1	10:15A, 8/30/67	10:15A, 8/31/67	4.32	10:15A, 8/31/67	10:15A, 9/1/67	4.32
2	10:30A, 8/30/67	10:30A, 8/31/67	4.12	10:30A, 8/31/67	10:30A, 9/1/67	4.12

Calc. 10 MGD

10.7 = 8.44

Observations and Remarks

Large sludge deposits have accumulated in the Pine River as a result of the $MgCO_3$ and $CaCl_2$ processes (Figure 2 and Figure 6-11; file copy). No attempt was made to measure the depth of this sludge, however, as revealed in the file copy photos these deposits extend approximately 150 feet into the river. Sludge deposits have also accumulated around the vicinity of outlet number 2 (Figure 4, file copy). Some of these deposits are yellow in color as of a sulfur compound. Others have the physical characteristics of water-softening zeolite.

Table 3 reveals that the pH of the wastewater at Outlet 2 is 2.0. This harsh acidity disintegrated the 1/64 inch thick aluminum flashing which was used to line the crest of the weir. This disintegration was noticed approximately 48 hours after the weir was installed.

Special attention should be focused on the chlorides and solids being discharged by this company. During the first survey 139 tons of chlorides and 5.9 tons of suspended solids were discharged. During the second survey the respective tonnages were 152.5 and 3.5.

Survey by: R. Caltrider, Sanitary Engineer
G. Kiimer, Sanitary Engineer
J. McDonald, Water Pollution Investigator
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Laboratory analyses by: R. Krueger, Chemist

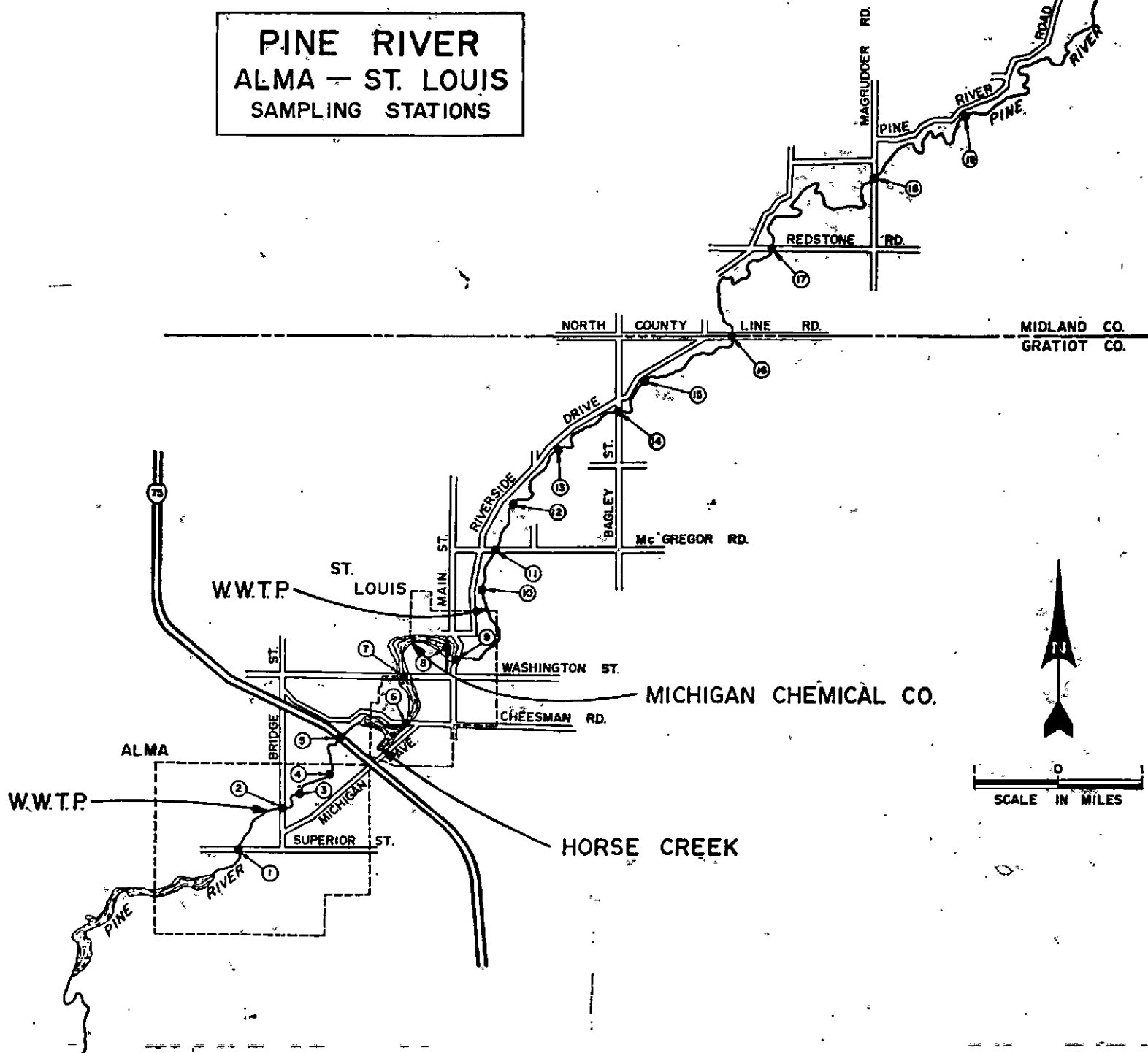
Plant management contact: Gary Larson

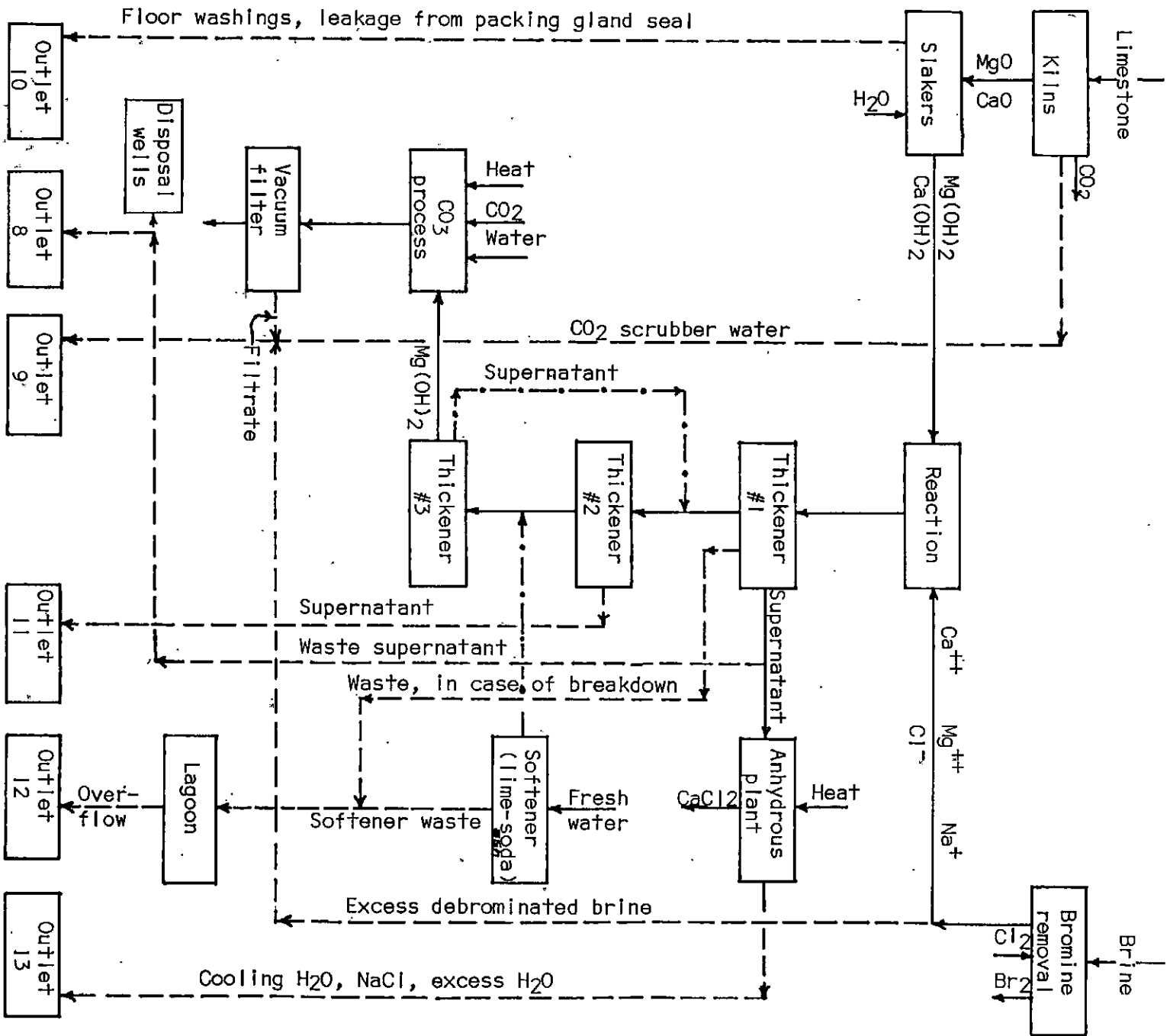
Report by: R. Caltrider
Water Quality Appraisal Unit
Michigan Water Resources Commission
March 19, 1968

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Note: An aerial view of the Company is available in the Water Resources Commission file.

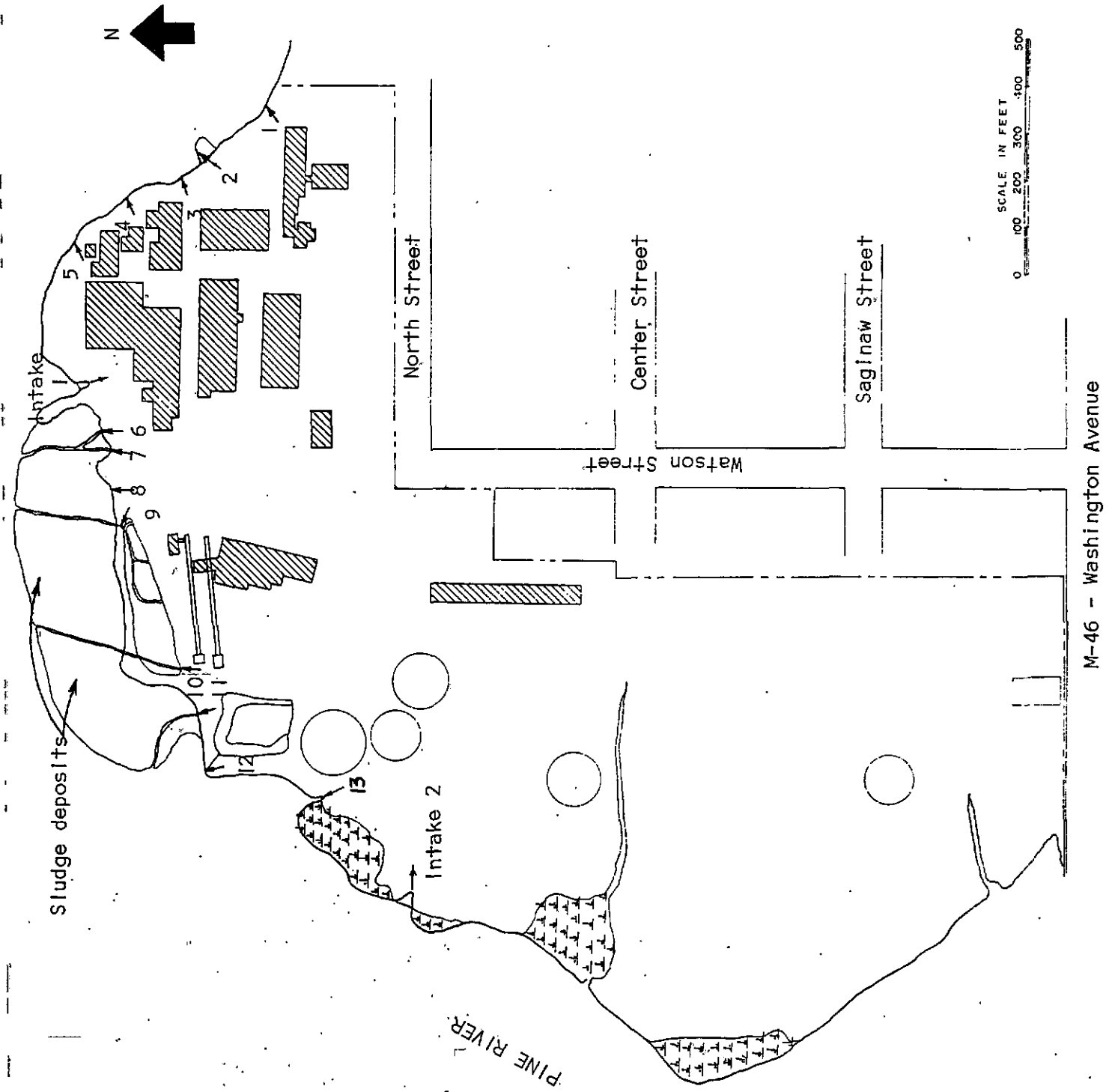
**PINE RIVER
ALMA - ST. LOUIS
SAMPLING STATIONS**





1. Schematic diagram of bromine, calcium chloride and magnesium carbonate processes, Michigan Chemical Company, St. Louis, Michigan, MWRC survey of week of August 28, 1967.

Figure 2. Map of Michigan Chemical Company, St. Louis, Michigan, including locations of inlets and outlets, MWRC survey of week of August 28, 1967.



M-46 - Washington Avenue