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Dissolved Heavy-Metal Removal by Insoluble Starch Xanthate (ISX)

Store below 40° F

Case-history studies demonstrate that very low residual-metal concentrations can be achieved in the treated effluents.

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ISX (insoluble starch xanthate), one of the simplest, most effective ways to reduce heavy metals in industrial wastewater, was originally developed at the U.S. Department of Agriculture, Northern Regional Research Center, Peoria, Illinois [1-7], under a grant from the Environmental Protection Agency. After internal ISX product research and development, Pollution Technology Systems of Garland, Texas announced formula changes that allow for mass-production capabilities, optimum heavy-metal uptake capacity, and the solution to shelf-life stability problems.

In January of 1980, ISX was introduced by Pollution Technology Systems as a commercially available product. ISX is allowing several industrial users to meet their present and future Public Owned Treatment Works (POTW), or Direct Discharge Statutory Water Quality Heavy Metal Limitations.

ISX offers industry a low-cost product requiring minimal capital investment for application of the treatment of industrial process and wastewater effluents. It is a highly cost-competitive product when compared to other known methods for final polish of process or effluent discharge water containing less than 10 mg/liter of heavy-metal ion contaminants in singular or complexed form.

ISX is a cereal grain-based product that is chemically cross-linked to make it insoluble in water and then xanthated to form an anionic polymer. When added to spent industrial process water containing dissolved heavy-metal cations, ISX exchanges sodium and magnesium ions upon contact for the heavy-metal cations.

Several case-history reports will follow, to show some of the ways ISX is being used to successfully remove toxic heavy metals from industrial process waters, thus allowing these industries to achieve the proposed Best Available Technology (BAT) and Best Practical Technology (BPT) discharge limits [8-9].

CASE HISTORY I

In 1980-1981, a large southeastern Company found it necessary to upgrade their waste-treatment plant in order to maintain compliance with their water quality-based direct discharge permit for heavy metals. (Table 1 defines the Company's operations.)

All process wastewaters are segregated in the manufacturing facility, then flow 400 meters to the segregated holding basins at the waste-treatment facility (Figure 1). Cyanide destruction occurs at pH = 10.5 with chlorine. After an approximate 90-minute contact time, the pH is lowered to 9.0 with additional chlorine to complete the destruction of cyanate to carbon dioxide and nitrogen.

Chromium (VI) is reduced to chromium (III) by the addition of sulfuric acid and SO_2. The reduction takes place at

TABLE 1. MANUFACTURING OPERATIONS

1. Printed circuit board fabrication
2. Aluminum and zinc die casting
3. Zinc plating
4. Chromium (VI) plating surface preparation
5. Copper-tin plating
6. Plastic injection molding
7. Chemical polishing and cleaning
8. Precious metal plating

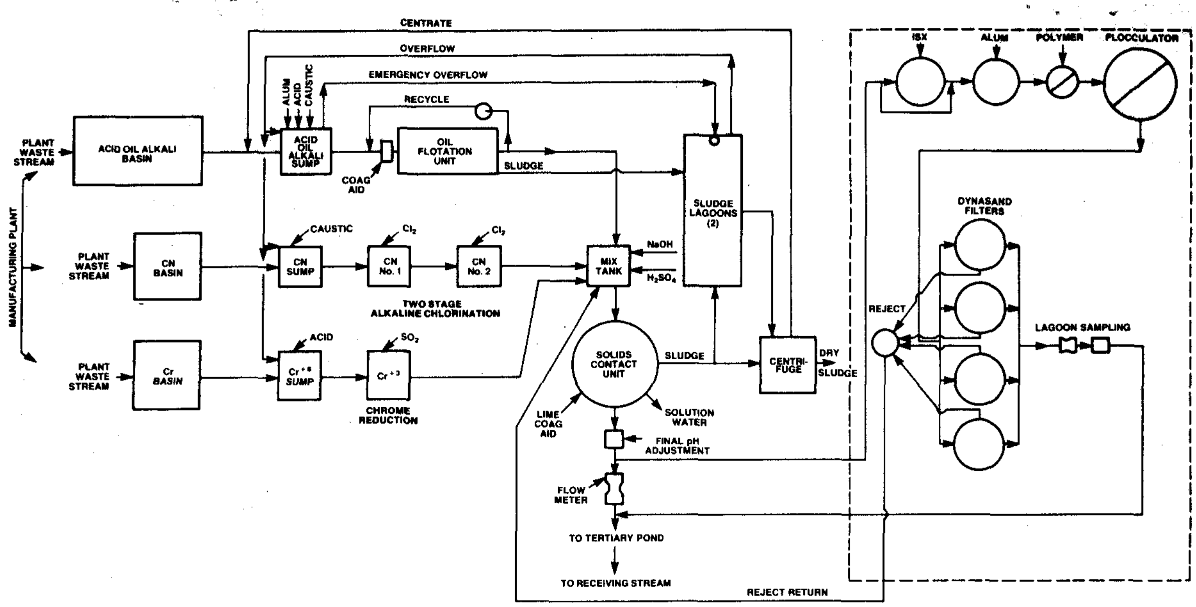

Figure 1. Waste-treatment facility.

pH 2.5 with a contact time of approximately 90 minutes. The alkaline/acid/oil waste stream is initially treated with alum to remove emulsified oil in a dissolved-air flotation (DAF) unit. All wastewaters from the three holding basins flow to the mix tank after initial treatment. The average initial copper concentration is 30-40 mg/liter unless plating-tank dumps are made, which will increase the copper and other metal concentrations from 100 mg/liter to as high as 1,000 mg/liter. The initial pH of around 6.0 is adjusted to 9.5-10 with caustic (25%) in the mix tank (40,000 liter). The wastewater then flows to the solids contact unit (300,000 liter lamella clarifier). Before the waste-treatment plant was upgraded in 1981, lime (227 kg/day) and an anionic polymer (3.6 kg/day) were metered into the contact unit to increase the pH and aid in solids formation settling. Now only 45 kg lime is required (pH = 10.5).

As the wastewater (1325 liter/min) leaves the clarifier the pH is adjusted to 7.0-8.0 with sulfuric acid (94%) and the copper concentration ranges from 0.5-5 mg/liter. Before 1981, the wastewater went to a holding pond before discharge to a tertiary pond, then on to a creek. Now, the water flows to the ISX contact tank prior to four continuously backwash sand filters.

ISX (23 kg) is premixed with water (1438 liter) in a 1500 liter tank. ISX (15.8 g/per min or 3 liter/min) is metered into the ISX contact tank. The ISX treated water gravity flows to the alum tank. Initial lab studies showed that alum was needed for better floc formation. However, under actual conditions, the alum addition is not necessary. Therefore, considerably less sludge is generated.

As the wastewater gravity flows to the polymer tank, cationic polymer (1 mg/liter) is added from the polymer premix tank (1.9 kg/1900 liter). The wastewater is pumped to a flocculator tank for conditioning before it flows through the four parallel sand filters.

The wastewater is analyzed every two hours for copper and other metal contact, usually (0.3 mg/liter), as it flows to the holding pond (Figure 2). The backwash from the sand filters is continuously returned to the mix tank and/or the clarifier.

The State discharge limit to the creek is 136 g (average) of any metal per day with a daily maximum of 272 g/day.

PLOT PLAN

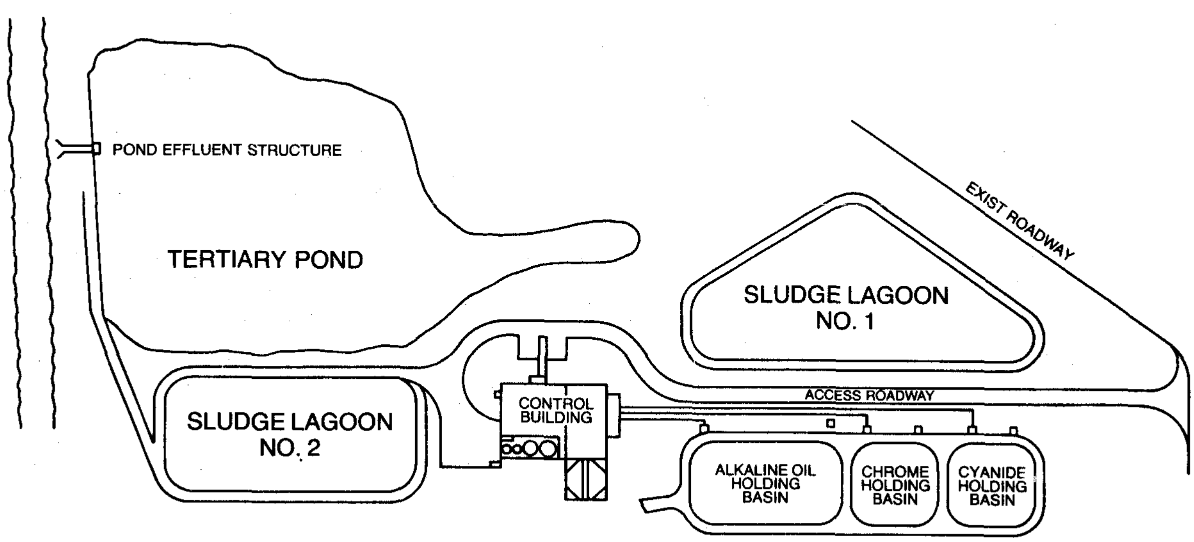

Figure 2. Plot plan.

Daily flows of 1.5 million liter/day with metal concentrations of approximately 0.08 mg/liter allow the company to meet its applicable discharge limits.

The sludge from the clarifier goes to one of two sludge lagoons. Periodically, it is pumped to the centrifuge following treatment with cationic and anionic polymer, and dewatered to 15% solids. The sludge is firm to the touch and is hauled to a Class 1 landfill. Company investigations are presently underway to delist the sludge.

Table 2 shows capital-cost information.

TABLE 2. CAPITAL-COST DATA

Total waste treatment plant	\$2,500,000
1981 2.6 × 10^6 liter/day capacity increase (Includes engineering, construction and capital-equipment installation)	\$ 700,000
ISX Related	\$ 22,000
2—Tanks—1500 liter	
2—Mixers	
2—Metering pumps	
1—Crane	
1—pH Controller	
Control-panel portion	
Walk-in refrigerator box	
Work paltform	
ISX slurry tank and mixer	
Acid-metering pump	

CASE HISTORY II

A Connecticut electroplating company, doing copper, chrome, and nickel plating, uses ISX on a precoated filter for a final polish. All plating processes have individual dead rinses, followed by two counter-flow rinses (Figure 3). Wastewaters are segregated for cyanide destruct with hypochlorite and chrome reduction with metabisulfite. All rinses, 410 liter/min, flow to a common sump for pH neutralization to 9.0 with caustic. The neutralized rinse water is transferred to combined holding and surge tanks (45,000 liter each), where it is continuously fed through two ISX (34 kg each) precoated filters for removal of metal hydroxides and heavy-metal cations. ISX treated water is returned to holding tanks for 90 percent rinse water recycle (Table 3).

TABLE 3. TREATED WATER

Metal	Initial Conc.,* mg/liter	ISX Treated Conc., mg/liter
Cr^{+3}	0.8	0.02
Cu^{+2}	7.0	0.02
Ni^{+2}	2.5	0.10

* Prior to ISX treatment

The ISX precoat is changed weekly. The sludge is hauled to a Class I landfill. All dead rinses are treated within the system on a weekly schedule. Recycling water has dramatically reduced water and sewage surcharge costs (90 percent). End-product quality control has been improved by the use of more stable rinse-water temperatures and known conditions, independent of climatic and source-water variations.

CASE HISTORY III

A Texas company uses ISX to remove residual cadmium before wastewater discharge. The rinse water (20 liter/min) is neutralized to pH 9 with caustic. The wastewater is then processed through a clarifier with upflow through an ISX sludge blanket. The treated effluent (Table 4) is discharged to a POTW after suspended solids removal with bag filters. The ISX usage is 6 kg every two weeks.

CASE HISTORY IV

A large Illinois communications equipment manufacturer recently upgraded its waste-treatment facility by installing an ISX metering system (capital cost = \$2,000). All

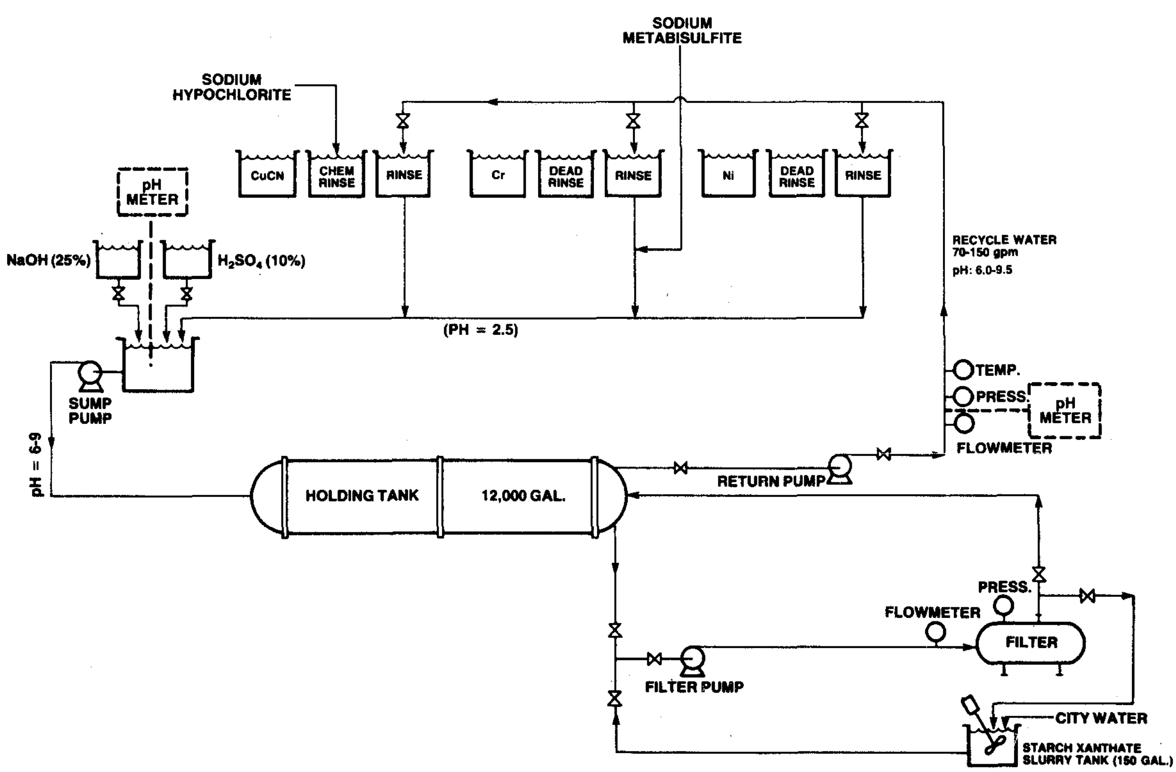

Figure 3. Waste Treatment Diagram.

TABLE 4. TREATED EFFLUENT

Metal	Initial Conc.,* mg/liter	ISX Treated Conc., mg/liter
Cd^{+2}	5.0	0.01

* Prior to ISX treatment

TABLE 5. TREATED EFFLUENT

Contaminant	Initial Conc.,* mg/liter	ISX Treated Conc., mg/liter
Cu^{+2}	6.0	0.5
Pb^{+2}	4.2	0.2
F^-	16.0	1.5

* Prior to ISX treatment

process waters (950 liter/min) are not segregated in the manufacturing plant, so the presence of complexing and chelating agents did prevent heavy-metal discharge limits from being achieved.

Process waters are neutralized to pH 9.5 with caustic, and ISX (154 mg/liter) in a water slurry is metered into the treatment system. A 45-minute contact occurs before solids removal on diatomaceous-earth precoated filters. The treated effluent (Table 5) is discharged to a POTW. Fluoride removal is an added benefit using ISX.

CONCLUSIONS

The cited examples show that ISX can be used in several different ways to achieve very low residual metal concentrations in treated effluent for discharge or reuse. Table 6 shows additional ISX treatment results that are being achieved by a cross-section of industrial categories. In addition to application in metal-finishing wastewaters, ISX is presently being evaluated for vanadium removal in boiler wastewaters from public utilities and as a selective flocculant in the recovery of sulfide-bearing ores.

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TABLE 6. CASE HISTORY RESULTS WITH ISX

Industrial Application	Flow Rate liter/min	ISX mg/liter	Dissolved Heavy-Metal Average Concentration, mg/liter					
			Cu^{+2}	Cd^{+2}	Ni^{+2}	Pb^{+2}	Zn^{+2}	Cr^{+3}
Aerospace	100	140						
Initial			0.12	0.44	2.7			1.86
ISX Treated			0.05	0.02	0.18			0.23
Brass Works	400	135						
Initial			6.5					
ISX Treated			0.2					
Electronic	1750	30						
Initial			1.25			0.50		
ISX Treated			0.05			0.02		
Printed Circuit Board	750	315						
Initial			6.0			4.2	4.0	
ISX Treated			0.05			0.6	0.01	
Oil Field Equipment	20	60						
Initial				5.0				
ISX Treated				0.01				
Electroplating	500	Pre-coat						
Initial			7.0		2.5			0.8
ISX Treated			0.02		0.10			0.02

Robert E. Wing obtained his B.A. in chemistry from Millikin University and his Ph.D. in chemistry from Southern Illinois University-Carbondale. He joined the Northern Regional Research Center in 1968 as a research chemist and has been working on the development of starch-based products for industrial applications. During the last 10 years he has developed several starch-based products which have found use as heavy metal scavengers in water pollution control. He has also developed several treatment processes effective for heavy metal removal from printed cricuit and plating on plastic rinse waters. He is a member of the American Electroplaters Society, American Chemical Society, and Sigma Xi and a part-time instructor at Bradley University. He has authored or co-authored 60 scientific papers and has 6 patents.