

PAPER

Electrocoagulation (CURE) Treatment of Ship Bilgewater for the U.S. Coast Guard in Alaska

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ABSTRACT

A wide variety of contaminants (i.e., heavy metals, suspended solids, colloids, oil) have been successfully removed from wastewater using various electrocoagulation systems. An innovative electrocoagulation system developed by Cleanup and Recovery (CURE) Corporation is described. The results of a field study for the U.S. Coast Guard (USCG) to treat 176,200 liters of bilgewater from two abandoned ships, La Pocena and Incentive, are presented. The CURE process was effective in removing oil and heavy metals (aluminum, boron, iron, and zinc) with removal efficiencies ranging between 71 and 99 percent. The mobility of the CURE equipment eliminated the need to transport the ship bilgewater for treatment off the island, which resulted in an estimated 90 percent (U.S. \$185,000) cost savings.

INTRODUCTION

One of the most important physiochemical unit operations used in water and wastewater treatment is the coagulation process. Coagulation is a process used to describe the destabilization and aggregation of smaller particles into larger particles. Wastewater contaminants such as ions (heavy metals) and colloids (inorganic and organic) are primarily held in solution by the electric charges. Schulze, in 1882, showed that colloidal systems could be destabilized by the addition of ions having a charge opposite to that of the colloid (Benefield et al., 1982). The destabilized colloids can be aggregated and subsequently removed by sedimentation and/or filtration.

Coagulation can be achieved by chemical or electrical means. Chemical coagulation is becoming less acceptable today because of the higher costs associated with chemical treatments (e.g., the large volumes of sludge generated). Electrocoagulation processes use electrical current (ac or dc) to neutralize ion and colloid charges and can replace and/or reduce the use of chemical agents (metal salts, polymer).

New equipment (CURE Electrocoagulation Tubes) used to treat ship bilgewater by the electrocoagulation process is described. A novel feature of the CURE system is the unique patented geometry (concentric anode and cathode tubes), which allows maximum removal of the contaminants by optimizing the design and operating control parameters. The results of a field investigation to treat

176,200 liters of bilgewater for the U.S. Coast Guard from two abandoned ships, *La Pocena* and *Incentive*, at Kodiak Island (near Anchorage, Alaska) are presented. The mobile CURE unit was operated for a 20 day period (August 10 to 30, 1992).

BACKGROUND

Description of CURE Process

A wide variety of contaminants (cations, anions, dissolved and suspended solids) have been removed from wastewaters (Table 1) using different electrocoagulation systems (Renk, 1989). These contaminants include heavy metals, such as cadmium, chromium, lead, and zinc; colloids, such as bacteria, oil, clays, carbon black, and silica; and other pollutants, such as phosphates. Various system geometries for the anode and cathode have been used, including plates, balls, fluidized-bed spheres, wire mesh, and rods (Figure 1). Identified disadvantages of these systems include higher capital and operating (power) costs and lower rates of flow.

The patented geometry (Figure 2) developed by Cleanup and Recovery (CURE) Corporation maximizes liquid surface contact between the anode and cathode (concentric) electrocoagulation tubes and minimizes the power requirements for efficient operation (Renk, 1989). The CURE system allows the wastewater to flow continuously through the cathode tube (negative voltage) causing a direct current flow to pass uniformly through the

FIGURE 1. Removal of total petroleum hydrocarbons. ND=non-detectable.

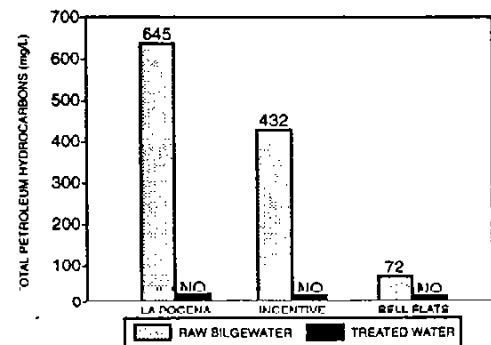
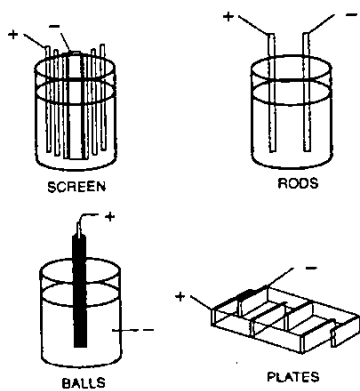


TABLE 1. Contaminant removal efficiencies for other electrocoagulation systems (Renk, 1989).

Contaminant	Reference	Raw	Concentration, mg/l	
			After Treatment	% Removal
<i>Dissolved Cations</i>				
Aluminum	Lee, 1975	60	0.01	99
Calcium	Rojo, 1979	46.5	10.0	78
Dadmium	Rojo, 1979	0.32	ND*	
Chromium, total	Lee, 1975	200	0.001	99
	Watanabe et al., 1977	100	<0.1	99
Copper	Rojo, 1979	0.8	ND	
	Rojo, 1979	6.3	ND	
	Lee, 1975	6.0	0.1	98
	Saburo et al., 1975	0.21	0.02	40
Iron	Rojo, 1979	65.0	ND	
Lead	Rojo, 1979	24.0	0.010	99+
	Saburo et al., 1975	0.05	0.01	80
Magnesium	Rojo, 1979	6.9	0.133	98
Manganese	Rojo, 1979	2.5	ND	
	Saburo et al., 1975	0.32	0.01	96
Mercury	Rojo, 1979	0.010	0.0005	95+
Nickel	Saburo et al., 1975	1.15	0.03	97
	Rojo, 1979	.235	ND	
Zinc	Lee, 1975	50	0.1	99
	Rojo, 1979	11.0	0.04	99+
	Saburo et al., 1975	1.64	0.08	95
<i>Dissolved Anions</i>				
Color	Rojo, 1979	800	10	98
Cyanide, Total	Lee, 1975	80	20	75
Fluoride	Rojo, 1979	1.1	0.415	62
Phosphate, as P	Rojo, 1979	3.8	1.1	71
<i>Other Dissolved and Suspended Material</i>				
Biochemical Oxygen Demand (BOD)	Ramirez et al., 1978	7,800	3,850	50
	Rojo, 1979	240	58	76
Oil and Grease	Nagendran et al., 1980	2,890	46	98
	Rojo, 1979	8,760	0.4	99
Total Organic Carbon (TOC)	Nickerson, 1982	11,000	30	99
	Ryan, 1989	630	10	98
Total Suspended Solids (TSS)	Nickerson, 1982	195,000	15	99
	Ramirez et al., 1979	4,475	95	98
	Rojo, 1979	2,594	12	99

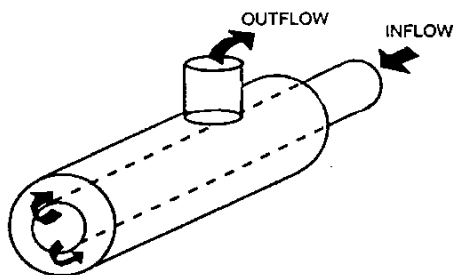
FIGURE 2. Various electrocoagulation geometries.



wastewater. The wastewater then passes through the annular space between the cathode and anode tubes. The liquid is thereby exposed to sequential positive and negative electrical fields (Figure 3). The polarity of the tubes is reversed periodically to assist in cleaning.

The principal cathodic reaction is the reduction of hydrogen ions to hydrogen gas ($2H^+ + 2e \rightarrow H_2$). The principal anodic reaction is the release of metal ions into solution (e.g., $Al \rightarrow Al^{3+} + 3e$). Anode tubes are sacrificed in the process. The anode materials (iron, aluminum); tube sizes, spacing and lengths; applied voltages and wastewater characteristics (pH, standard redox potential, conductivity) can be varied and optimized for maximum removal efficiencies of specific contaminants. Oxidants, reductants,

FIGURE 3. CURE electrocoagulation tubes.



polymers, and other chemicals can be introduced to assist in the coagulation process. After the treated wastewater leaves the electrocoagulation tubes (less than 20 seconds retention time), the destabilized colloids are allowed to flocculate and are then separated in an integrated clarifier system. Sometimes polymers are added in the clarifier to enhance flocculation, but in most cases they are not required. The sludge from the clarifier can be further dewatered using a filter press, settling pond, or other dewatering techniques.

The Western Research Institute (WRI) has treated numerous wastewaters (electroplating, acid drainage, foundry, and oil brine) using the CURE Process. Results indicate that this process is capable of removing 95 to 99 percent of heavy metals (such as cadmium, chromium, lead, nickel, and zinc), oil (emulsified), and colloids (bacteria, color, dyes) (Renk, 1989). The toxicity of certain tar sand processing waters has also been reduced by the CURE process (Renk, 1988).

WRI test results showed that the CURE process can form stable acid-resistant sludges if sufficient activation energy is supplied (Renk, 1989). For example, nickel has been precipitated as nickel iron oxide (NiFe_2O_4), which is more stable than nickel oxide (NiO) or nickel hydroxide ($\text{Ni}(\text{OH})_2$) when subjected to acid conditions. The latter two oxides are typically formed by chemical addition.

U.S. Environmental Protection Agency (EPA) tests performed on a CURE generated

electroplating sludge (chromium and cadmium) also passed the Toxic Classification Leaching Procedure (TCLP) and showed that heavy metals did not leach from the sludge when subjected to acid conditions (Renk, 1989). This allowed the sludge to be re-classified as non-hazardous. Other electrocoagulation processes have reported similar results (Franco, 1974; Watanabe and Nojiri, 1975; Duffey, 1983).

Ship Bilgewater Characteristics

Typical bilgewater contains oil in the free, emulsified, and dissolved states. Other contaminants include heavy metals, high suspended solids, and high surfactants (created by microbial activities and cleaning operations).

Free or bulk oil exists as a continuous layer floating on top of the aqueous phase and usually consists of a mixture of fuel, hydraulic, and lubrication oils (Verdegan and Jaisinghani, 1980). Emulsified oil consists of fine oil droplets (less than 10 microns in size), which are usually dispersed in the oil phase by the presence of surfactants. Concentrations in the range of 50 to 1,000 mg/l (extractable oil) have been observed in ship bilgewater (Osamor and Ahlert, 1978). Dissolved oil (hydrocarbons) may also be present and cannot be removed by physical separation methods.

Typical bilgewater characteristics (Table 2) indicate that the water phase is characterized by a slightly acidic pH (due to microbial activity), high suspended solids, and high extractable oil concentrations. Extractable oil concentrations (with a mean of 176 mg/l) were observed for samples taken from U.S. Coast Guard (salt water) vessels. The mean of the Zeta potential, the surface charge on the emulsified oil droplets, was measured as -4.9 mV and -44.8 mV in salt and freshwater, respectively (Verdegan and Jaisinghani, 1980).

The USCG requires that effluent discharges of ship bilgewater contain less than 5 mg/l of oil. It is evident that to comply with the regulation most of the emulsified/dissolved oil must be removed. Test results at WRI indicated that the CURE process can destabilize oil emulsions resulting in oil removal efficiencies of between 93 and 99 percent (Renk, 1989).

Alternate Bilgewater Treatment Systems

A variety of technologies have been employed in the treatment of ship bilgewater. Conventional treatment systems use gravity oil/water separators, cartridge filter/coalescers, and/or regenerative filter coalescers. The design and operation of each system is dependent on the physical and chemical characteristics of the ship bilgewater to be treated.

TABLE 2. Typical bilgewater characteristics (from Verdegan and Jaisinghani, 1980).

PARAMETER	MEAN	RANGE
pH	6.7	4.5-9.1
Conductivity ($\mu\text{ohms/cm}$)	6024	80-41,000
Suspended Solids Greater Than 0.3 μm (mg/l)	314	18-1,410
Extractable Oil (mg/l)	176	3-1,161
Zeta Potential (mV)	-14.7	+16.2-46.5

Gravity separators are primarily used to separate free or bulk oil and are less effective for stable oil emulsions. It has been shown that viscous oil can also form oil blockages in the plate separators, which can result in the formation of a dense oil water foam (Jaisinghani and Sprenger, 1979).

Cartridge filter/coalescers do not perform well in treating ship bilgewater, which is high in suspended solids. Skewes (1976) has reported that the efficiency and life of the cartridge filter/coalescer is reduced, resulting in higher replacement and operating costs.

FIELD CASE STUDY

Project Description

In August 1992, the USCG in Alaska approved the use of the CURE system for the treatment of ship bilgewater at Kodiak Island near Anchorage, Alaska. The ship bilgewater, collected from two abandoned vessels (*La Pocena* and *Incentive*), was stored in tanks at three different locations across the Island (64 km/40 mile radius).

The ship bilgewater (176,000 l/46,500 gal) was contaminated with high concentrations of oil, suspended solids, and heavy metals. Approximately 101,250 l (26,750 gal) from *Incentive* and 74,750 l (19,750 gal) from *La Pocena* were treated near the harbor and at Bell Flats, respectively. Prior to treatment, the bilgewater from *La Pocena* was stored for six months longer than that from *Incentive*. Hydrogen sulfide odors were present in the bilgewater from the former vessel, indicating the presence of sulfate reducing bacteria.

The treatment criteria established by the USCG was to reduce the oil concentrations (extractable hydrocarbons) to less than 5 mg/l. The licensed contractors, Premier Environmental and VRCA Environmental, used a mobile CURE treatment unit, thus eliminating the need to transport the bilgewater to a larger treatment facility (off the island). The estimated cost of transporting and disposing the wastewater to this facility was approximately U.S. \$210,000 (\$1.19 per liter).

Equipment and Methods

Site assessments and preliminary treatment tests were conducted for evaluation by the USCG prior to commencing the project. The CURE unit and power generator were mounted in an enclosed van to facilitate movement to each treatment site. Approximately 15,141 liters were treated each day. Fifty percent of the operating time (20 days) was associated with mobilization/demobilization of the CURE equipment to and from each site.

The CURE unit was calibrated and the optimum treatment control parameters were determined prior to each treatment run. A small (7.0 to 23.0 l/min) variable drive, progressive cavity feed pump (17.3 KPa) was used and operated at maximum flow throughput. Two anode electrocoagulation tubes (aluminum and iron) were used in the treatment process.

Effluent samples were taken following treatment through the CURE unit and taken prior to entering the 1,136 liter clarifier. Because of the small clarifier the sedimentation retention time was only 50 minutes. Normally four hours is required. Consequently, an anionic polyacrylamide polymer was added (1.2 mg/l) as a coagulant aid.

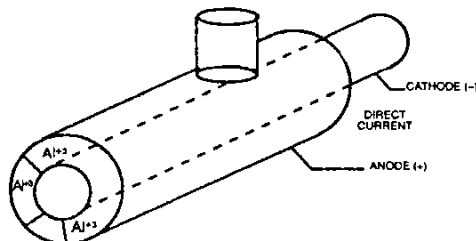
Following the clarifier, the effluent passed through activated carbon filters for final polishing and removal of any trace hydrocarbons. Samples were taken and analyzed for total petroleum hydrocarbons and heavy metals. The treated effluent was stored in tanks, and ultimately discharged back into the harbor. The method of discharge and acceptable quality of treatment was approved by the USCG for each site.

RESULTS AND DISCUSSION

Raw and treated bilgewater samples were analyzed by an independent laboratory (Chemical and Geological Laboratory) for total petroleum hydrocarbons according to EPA method 418.1. Heavy metal and other cations/anions were analyzed according to EPA method 2007. All samples were slightly acidic with pH values in a range between 6.0 and 8.0.

Total petroleum hydrocarbons (TPH) in the raw bilgewater ranged from 72 to 646 mg/l. These values agree with "typical" emulsified oil concentrations reported by others (see Table 2). The TPH values for the treated samples (see Figure 4) were below the detection limit of 0.2 mg/l. These results verify that the CURE

FIGURE 4. Anode reaction: $\text{Al (metal)} \rightarrow \text{Al}^{+3} + 3 \text{ electrons}$.



process is effective in destabilizing oil emulsions. Removal efficiencies were shown to exceed 99 percent.

A summary of contaminant removal efficiencies for raw and treated bilgewater samples taken at Bell Flats (*La Pocena*) is shown in Table 3. The removal efficiencies of heavy metals (aluminum, boron, iron, and zinc) ranged between 71 and 99 percent (see Table 3). Removal efficiencies of the dissolved cations, such as calcium, sodium, and potassium, ranged between 23 and 53.2 percent. WRI test results also indicated that the electrocoagulation process does not remove these cations efficiently (Renk, 1989). It was interesting to note that the removal efficiency of phosphorous (73.4 percent) was also similar to a value obtained by Rojo (1979) (see Table 1).

Following CURE electrocoagulation treatment, the volume of bilgewater was reduced from 176,000 liters to less than 2,270 liters of sludge, a 98 percent volume reduction. The sludge from each location was placed in drums and transported to a treatment facility for disposal. The cost of final bilgewater treatment (including labor, equipment, and energy) was estimated at less than U.S. \$0.12/liter. This is approximately 10 percent of the normal disposal cost associated with transporting and treating bilgewater in a larger facility off the island.

Power consumption was found to be below that associated with the treatment of fresh water due to the higher conductivity of seawater.

CONCLUSIONS

The results of the field study show that electrocoagulation (CURE) treatment is effective in destabilizing oil emulsions. Removal efficiencies (extractable oil) exceeded 99 percent resulting in non-detectable values of less than 0.2 mg/l TPH values in the effluent.

The CURE process was also effective in removing heavy metals (aluminum, boron, iron, and zinc) with removal efficiencies ranging between 71 and 99 percent. However, the process was less effective in removing cations such as sodium and potassium which do not form a precipitate.

The volume of ship bilgewater, following CURE treatment, was reduced by 98 percent, from 176,000 liters to less than 2,270 liters of sludge.

The mobility of the CURE equipment eliminated the need to transport the bilgewater for treatment off the island resulting in an estimated cost savings of U.S. \$185,000. The average cost of treating the bilgewater on-site, estimated at U.S. \$0.12/liter was approximately 10 percent of the cost for treatment off the island.

It is important that the ship bilgewater be characterized and the CURE equipment be calibrated to establish optimum design and operating control parameters. These parameters include the selection, size, and spacing of the tube materials; the evaluation of power requirements; and the addition of coagulant aids.

REFERENCES

- Benefield, L.D., Judkins, J.F. and Weand, B.L. 1982. *Process Chemistry for Water and Wastewater Treatment*. Prentice-Hall Inc., p. 212.
- Duffey, J.G. 1983. *Electrochemical Removal of Heavy Metals from Wastewater, Product Finishing*, p. 72, August 1983.
- Franco, N.B. 1974. *Electrochemical Removal of Heavy Metals from Acid Mine Drainage*. Environmental Protection Agency Report EPA-67012-74-023. May 1974.
- Herbst, B. and Renk, R.R. 1989. Electrolytic treatment of liquids. U.S. Patent No. 4,872,959. Oct. 10, 1989.
- Jaisinghani, R.A. and Sprenger, G.S. 1979. A study of oil water separation in corrugated plate separators. *J. of Eng. for Industry*, vol. 101, no. 4, November 1979, pp. 441-448.
- Nagendran, J. and Hruday, S.E. 1980. Oil recovery and recycled water treatment for in situ oil sand production. Environmental and Economic Considerations in Energy Utilization. In: *Proceedings of the Seventh National Conference on Energy and the Environment*. Phoenix, AZ. p. 69.
- Nickerson, F.H. 1988. Electrical coagulations: A new process for preparing plant water treatment. *Coal Mining and Processing*, 19(9):64-67.
- Osamor, F.A. and Ahlert, R.C. 1978. Oil/Water Separation: State-of-the-Art. Environmental

TABLE 3. Contaminant removal efficiencies for *La Pocena*.

CONTAMINANT	Concentration (mg/l)		% Removal
	Untreated	Treated	
PETROLEUM HYDROCARBONS			
Petroleum Hydrocarbons	72.5	ND (0.2)	99*
HEAVY METALS			
Aluminum	4.16	0.74	82
Boron	4.86	1.41	71
Iron	95.40	ND (1.0)	99*
Zinc	3.41	ND (0.5)	99*
DISSOLVED CATIONS			
Calcium	293	137	53.2
Magnesium	943	300	68.2
Manganese	0.93	ND	99*
Sodium	8690	5770	33.6
Potassium	287	222	23.0
DISSOLVED ANIONS			
Phosphorous	5.38	1.43	73.4

- Protection Agency Report EPA-600/2-78-069, April 1978.
- Ramirez, E.R. and Clemens, O.A. 1978. Physicochemical treatment of rendering wastewater by electrocoagulation. In: *Proceedings of the Ninth National Symposium of Food Processing Waste*. Denver, CO. EPA-600/2-78, p. 264.
- Renk, R.R. 1988. Electrocoagulation of tar sand and oil shale wastewaters. *Energy Progress* (4), pp. 205-208.
- Renk, R.R. 1989. Treatment of hazardous wastewaters by electrocoagulation. In: 3rd Annual Conference Proceedings (1989). Colorado Hazardous Waste Management Society.
- Rojo, S.A. 1979. Apparatus for removing impurities from wastewater. U.S. Patent No. 4,149,953. April 16, 1979.
- Ryan, P. 1989. Electrocoagulation. *HazTech News*, June 29, 1989, p. 96.
- Saburo, M., Hiroyoshi, I., Hisorumi, W. and Hiromasa, M. 1975. Coagulation treatment plant for wastewater. West German Patent, *West German Offenlegungsschrift*. 24(61),943.
- Skewes, R.L. 1976. USCG Oily Water Separator System Cartridge Usage Data Survey. U.S. Coast Guard Report USCG-D-40-76.
- Verdegan, B.M. and Jaisinghani, R.A. 1980. Field study of bilgewater and its implications for separator evaluation. *Mar. Technol.*, October 1980, pp. 76-80.
- Watanabe, Y. and Nojiri, N. 1977. Electrolytic treatment of wastewaters. U.S. Patent No. 4,014,766. March 29, 1977.