United States
Environmental Protection
Agency

EPA/540/S-93/504
September 1993

SUPERFUND INNOVATIVE
TECHNOLOGY EVALUATION

Emerging Technology Summary

Electro-Pure Alternating Current Electrocoagulation

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The Superfund Innovative Technology Evaluation (SITE) Program was authorized as part of the 1986 amendments to the Superfund legislation. It represents a joint effort between the U.S. Environmental Protection Agency's (EPA) Office of Research and Development and Office of Solid Waste and Emergency Response. The program is designed to assist and encourage the development of waste treatment technologies that would contribute innovative solutions to our hazardous waste problems. Under the Emerging Technology portion of the SITE Program, a 2-yr research effort was conducted by Electro-Pure Systems, Inc., to evaluate the technical and economic feasibility of alternating current electrocoagulation (ACE) for remediation of aqueous waste streams at Superfund sites.

The ACE Technology introduces low concentrations of nontoxic aluminum hydroxide species into the aqueous media by the electrochemical dissolution of aluminum-containing electrodes or pellets. The aluminum species that are produced neutralize the electrostatic charges on suspended material and/or prompt the coprecipitation of certain soluble ionic species, and thereby facilitate their removal.

Electrocoagulation has been demonstrated to enhance the filtration and dewatering rates for solids removed from an effluent; such enhancements are prompted by growth in the mean particle size from typically <0.3 µm in diameter to as much as 150 µm, depending on the degree of electrocoagulation. Significant reductions in the total suspended solids (TSS) loading of particulate slurries and in the concentrations of metals (lead, copper, zinc, chromium), fluorides, and phosphates from aqueous streams can be achieved under certain pH conditions. Treatment does not entail adding chemicals (polymers, metal salts, polyelectrolytes) whose accumulation might inhibit reuse of the effluent as process water. Rather, the insoluble aluminum hydroxide resulting from electrocoagulation may be removed by standard filtration practices.

This Summary was developed by EPA's Risk Reduction Engineering Laboratory, Cincinnati, OH, to announce key findings of the SITE Emerging Technology Program that is fully documented in a journal article (see ordering information at back).

Introduction

Chemical coagulation has been used for decades to destabilize colloidal suspensions and to effect precipitation of soluble metal species as well as other inorganic species from aqueous streams, thereby permitting their removal through sedimentation or filtration. Alum, lime, and/or polymers have been the chemical coagulants used. These processes, however, tend to generate large volumes of sludge with a high bound-water content that can be slow to filter and difficult to dewater. These treatment processes also tend to increase the total dissolved solids content of the effluent, making it unacceptable for reuse within industrial applications.

The ACE Technology was originally developed in the early 1980s to break stable aqueous suspensions of clays and coal fines produced in the mining industry. Traditionally, these effluents were treated with conventional techniques that made use of organic polymers and inorganic salts to agglomerate and enhance the removal of the suspended materials. This ACE Technology was developed to simplify effluent treatment, realize cost savings, and facilitate recovery of fine-grained coal.

ACE Technology is based upon colloidal chemistry principles–principles using alternating electrical power and electrophoretic metal hydroxide coagulation. The basic mechanism for the technology is electroflocculation wherein small quantities (generally <30 mg/L) of aluminum hydroxide species are introduced into solution to facilitate flocculation. Electroflocculation causes an effect similar to that produced by the addition of chemical coagulants such as aluminum or ferric sulfate. These cationic salts destabilize colloidal suspensions by neutralizing negative charges associated with these particles at neutral or alkaline pHs. This enables the particles to come together closely enough to agglomerate under the influence of van der Waals attractive forces. See Figure 1 for the ACE basic process flow.

Although the electroflocculation mechanism resembles chemical coagulation in that cationic species are responsible for the neutralization of surface charges, the characteristics of the electrocoagulated floc differ dramatically from those generated by chemical coagulation. An electrocoagulated floc tends to contain less bound water, is more shear resistant, and is more readily filterable.

Application of an AC electric field to the electrodes induces dissolution of the aluminum and formation of the polymeric hydroxide species. Charge neutralization and particle growth are initiated within the electrocoagulation cells and continue following discharge of the aqueous medium from the apparatus. (In this way, product separation into solids, water, and oils may be achieved.)

The ACE Technology was tested using two designs of the ACE Separator™: (1) a parallel electrode unit in which a series of vertically oriented aluminum electrodes form a series of monopolar electrolytic cells through which the effluent passes and (2) a fluidized bed unit with nonconductive cylinders equipped with nonconsumable metal electrodes between which a turbulent fluidized bed of aluminum alloy pellets is maintained. In the fluidized bed unit, introduction of compressed air into the electrocoagulation cells assists in maintaining the turbulent fluidized bed and in enhancing the aluminum dissolution efficiency by increasing the anodic surface area. Typically, the fluidized bed unit dissolves aluminum at least one order of magnitude more efficiently than does the parallel electrode unit.

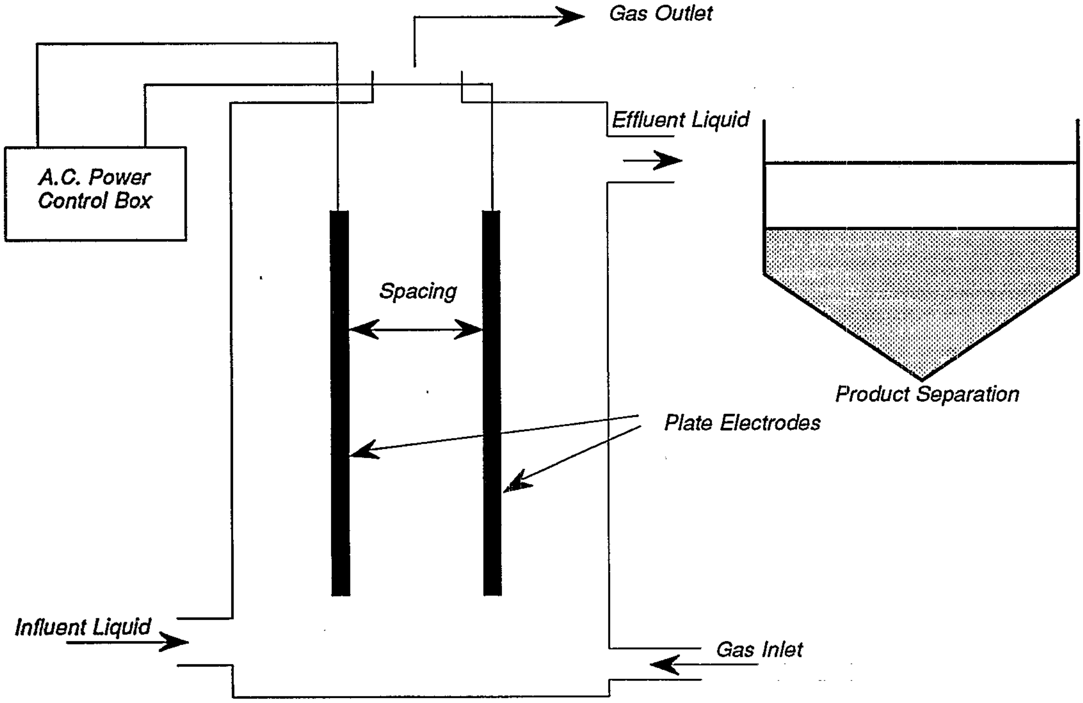

Figure 1. *Schematic of an ACE Separator™ used in alternating current electrocoagulation.*

Electrocoagulation operating conditions are highly dependent on the chemistry of the aqueous medium, especially conductivity. Other influent characteristics such as pH, particle size, and chemical constituent concentrations will influence operating conditions. Treatment generally requires application of low voltage (<150 VAC) to the electrocoagulation cell electrodes; current usage is typically 1 to 5 amp-min/L. The flow rate of the aqueous medium through an electrocoagulation cell depends on the solution chemistry (conductivity), the nature of the entrained suspension or emulsion, and the extent of electrocoagulation required to achieve the treatment objective. Retention times as short as 5 sec are sometimes sufficient to break a suspension. Electrocoagulation may be accomplished in a single pass or multiple passes (recycle mode). In the fluidized bed unit, a mechanical scrubbing action is created within the electrocoagulation cell–an action that reduces buildup of impermeable oxide coatings on the aluminum pellets and the inherent loss of efficiency that would result. Depending on system configuration, maintenance of the apparatus is limited to periodic replenishment of the aluminum fluidized bed material and/or electrodes. For most applications, pellets for the fluidized bed unit can be produced from recycled aluminum scrap or beverage containers. Where sludge reclamation is the objective, however, the use of higher quality pellets is required to reduce the introduction of impurities into the sludge.

This summary describes the research effort associated with bench- and pilot-scale testing of various surrogate wastewaters for determining the optimum operating conditions, treatment effectiveness, and cost of treatment.

Experimental

EPA's SITE Program research entailed testing the ACE Technology (in both the parallel electrode and fluidized bed system configurations) on various surrogate wastes containing emulsified diesel fuel, metals, and clays. The wastes were prepared to resemble those of leaking, underground storage tanks and soil washing operations. The primary testing objective of such testing was to establish optimum operating conditions for the ACE Separator™ to break the oil/water emulsion and achieve reductions in clay suspended solids and soluble metal pollutant loadings. Experiments were conducted on surrogate wastes prepared by mixing 0.2 to 3.0 wt. % of the -230 mesh (clay and silt) fraction of the EPA's Synthetic Soil Matrix (SSM) with 0.5 to 1.5 wt. % Number 2 diesel fuel, with 0.05 to 0.10 wt. % of an emulsifier (Titon-100X* or Alconox soap), and with from 10 mg/L to 100 mg/L of one or more of the following contaminants: copper, nickel, zinc, orthophosphate, or fluoride. The pH of each surrogate mixture was adjusted with either sodium hydroxide or calcium oxide to the desired value (5, 7, or 9) and the conductivity raised to roughly 1200 microSiemens per centimeter (µS/cm) to 1500 µS/cm with sodium chloride to simulate values expected in nature.

Initially, bench-scale electrocoagulation experiments using the parallel electrode unit were conducted on five aqueous-based systems that included a metals mixture, a clay suspension, a diesel fuel emulsion, a soluble organic solution, and a diesel fuel/soluble organic emulsion. The operating conditions determined during the Year One SITE work effort were used as the conditions for these tests. Optimum treatment time was established by examining the trend in contaminant loadings as a function of treatment time. To compare the results with conventional treatment processes, aliquots of each surrogate stock solution were treated with alum. Sufficient alum was added to give the aluminum equivalent to that introduced in the electrocoagulation experiments.

During the Year Two investigations, operating difficulties, persistent electrode coating and fouling, and low efficiencies of aluminum generation prompted including the alternative, fluidized-bed, electrocoagulation cell design in the remaining bench- and pilot-scale testing program. Three phases of laboratory experiments were undertaken to evaluate both electrocoagulation units: (1) preliminary screening experiments to demonstrate the feasibility of reducing the concentration of each metal, (2) matrix experiments to define the most opportune retention time and current (or current density), and (3) optimization experiments to define other ACE Separator™ operating parameters to achieve the most cost-effective removal conditions. The pH was adjusted to 5, 7, or 9 and the conductivity raised to approximately 1200 µS/cm with sodium chloride. The conductivity of some surrogate wastes was increased to approximately 3000 µS/cm and subjected to electrocoagulation. Surrogate wastes subjected to these experiments included the five aqueous systems described above as well as surrogate wastes containing individual constituents such as nickel, zinc, copper, fluoride, and phosphate.

Pilot-scale tests were performed by using both the parallel and fluidized bed configurations of the ACE Separator™. A 12-hr experiment using the ACE Fluidized Bed Separator™ was conducted on 208-L batches of surrogate waste solution containing 0.2 wt % SSM fines, 0.5 wt % diesel fuel, 0.05 wt % Alconox surfactant, and 10 mg/L each of Cu^{2+}, Zn^{2+}, PO_4^{3-}, F^-, and Ni^{2+}, and whose conductivity and pH had been raised to 1200 µS/cm and 7, respectively. This surrogate was recycled through a 4-in.- diameter, Schedule 80, PVC pipe, 24-in.-high pilot-scale ACE Separator™, which was equipped with two Type 316 stainless-steel electrodes (24 in. high, 2.5 in. wide) and whose interior was filled with 8 to +16 mesh aluminum pellets. The unit was powered at a constant 20 amp, and the voltage was allowed to vary as the electrocoagulation treatment progressed over the 12-hr period. In this experiment, the flow of the surrogate solution through the ACE Separator™ was varied from 1 to 6 gpm and the quantity of compressed air introduced into the solution feed line ranged up to a maximum of 10 psig. Samples of the surrogate solution were collected at various times throughout the experiment to document the rate of aluminum ion generation and the reductions in concentration of the metal contaminants, chemical oxygen demand (COD), and TSS.

In a similar pilot-scale test using the parallel plate unit, the surrogate waste was composed of essentially the same constituents as that for the fluidized bed experiment. The notable changes were that the conductivity of the solution was increased to approximately 3,000 µS/cm and no fluoride salt was added. The other operating parameters were based on results obtained from the bench-scale tests. The aluminum generation and consumption rates and the electrical power required to effect acceptable phase separation as well as contaminant reductions were monitored.

Throughout the various phases of the experimental program, samples of the treated effluent were collected and allowed to settle for 30 min. The supernate was removed and analyzed. The subnate, containing the settled floc, was filtered and the filtrate and filter cake analyzed.

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* Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

Results and Discussion

Optimum Operating Conditions

Optimum operating conditions for the parallel electrode unit were developed from these studies (Table I). These conditions served as the basis for the subsequent pilot-scale tests.

Optimum operating conditions for parallel electrode unit as a result of bench-scale tests were electrode spacing 0.5 in.; current, 4 amps; retention time, 3 to 5 min; frequency, 10 hertz; and fully submerged.

Similarly, based on the bench-scale testing of the fluidized bed design, the optimum operating conditions established were electrode spacing, 1-in.; aluminum pellets size, 8 to +16 mesh; and, current, 20 amps.

Treatment Effectiveness

Based upon bench-scale experiments conducted on the EPA surrogate wastes, the following summarizes the findings:

- When compared with alum treatment, electrocoagulation provided approximately 83% less sludge volume and a 76% improvement in filtration rate
- For the fluidized bed configuration, aluminum or stainless steel may be used as electrode material in the system, with comparable results
- With both increased frequency for the AC and increased retention time, the agglomerated particles tend to disaggregate.

Pilot-scale tests were conducted with the use of both the parallel and fluidized bed configurations of the ACE Separator™ on a 3% soil slurry containing roughly 50% clays, 1.5% diesel fuel, and 0.1% of a strong surfactant. Electrocoagulation reduced the TSS (222 mg/L to 4.5 mg/L) and total organic carbon (TOC) (130 mg/L to 6.6 mg/L). Copper was reduced by 72%, cadmium by 70%, chromium by 92%, and lead by 88%. No appreciable change in total solids (TS) loadings in the supernate resulted from electrocoagulation.

Table 1. Optimum Operating Conditions for Parallel Electrode Unit Based on Bench-Scale Tests

Parameter	*Value*
Current	*4 Ampere*
Electrode Spacing	*0.5 Inches*
Retention Time	*3 to 5 Minutes*
Frequency	*10 Hertz*
Submergence	*Fully Submerged*

Particle size was enhanced by the clay fraction as a result of electrocoagulation. The mean particle diameters of the ACE Separator™ treated particulates, both in the supernate and the filtrate (188 µm and 230 µm, respectively), increased by a factor of approximately 85 and 105, respectively, over that in the original slurry (2.2 µm).

Data obtained from the 12-hr, pilot-scale, fluidized bed test showed that after 30 min of treatment, more than 90% of the metals and phosphates were removed. Aluminum generation rates were highest when the throughput flow rate was <4 gpm. This upper flow limit may reflect compaction of the fluidized bed aluminum pellets against the upper screen of the electrocoagulation cell, thus placing them out of the range of the electrodes. As the emulsion is destabilized, the surrogate solution most likely becomes less resistive to ion mobility and, thereby, improves the operational efficiency of the ACE Separator™.

Filtration time for solids coagulated from particulate suspensions and oily emulsions by electrocoagulation is much less than for solids formed by chemical coagulant addition. Slurries tested were treated with alum addition and with an ACE Separator™. Electrocoagulation improved the filtration rate of titanium oxide by 63%. Other examples (for an oily emulsion and for biological sludge) indicate highly enhanced filtration rates for ACE Separator™ treated waste streams when compared with those of either untreated or alum-treated waste streams.

Shear strength of an electrocoagulation floc is generally much greater than the shear strength of an alum floc. Both sonic treatments (used to evaluate the structural integrity of the floc) and actual filtration tests demonstrated higher shear strength of the electrocoagulation flocs.

Electrocoagulation of metal and phosphate-bearing industrial solutions indicates excellent nickel, copper, and phosphate concentration reductions. More than 90% (concentration basis) of phosphate and copper can be removed from such solutions at low aluminum and electrical power requirements. Reduction in the nickel concentration varies between 75% and 85% (concentration basis).

Electrocoagulation of synthetic laboratory solutions and industrial wastewater also confirmed the feasibility of utilizing electrocoagulation for phosphate removal. Treatment of effluent from a commercial laundry reduced the phosphate concentration from 45 mg/L to 5.4 mg/L after low-intensity electrocoagulation (0.36 kW, 0.75-min retention time). Electrocoagulation of process water from a phosphate mining operation reduced the phosphate level by 91%, from 160 mg/L to 14 mg/L (3.3 kW, 0.17 min). Finally, treatment of dilute phosphoric acid solutions with a nominal 100 mg/L total phosphate concentration and a conductivity of approximately 2000 µS/cm resulted in >95% reductions in soluble phosphate over a range of acidities.

Capital and Operating Costs

As part of this research effort, projected treatment cost estimates were developed. Overall treatment operating costs (electricity, aluminum pellets, operation, and maintenance) will vary upwards from $0.50/1000 gal, depending on emulsion strength, unwanted component concentration(s) (for example, emulsifiers) in the effluent, and its TSS. (It should be noted that, at the outset, we established that operating conditions exceeding $3.00/1000 gal would not be competitive with conventional treatment processes, and thus, they were eliminated from future testing consideration.) Estimates are based on bench- and pilot-scale testing, additional considerations may be involved in full scale operation.

Operator supervision and maintenance would be limited to periodic replenishment of the aluminum pellets, chemical pretreatment systems (for example, salt addition for conductivity enhancement), and electrode replacement. Estimated operating costs are based on laboratory and limited pilot-scale testing of effluents, and currently these costs exceed those for comparable traditional chemical treatment (alum or polyelectrolytes). The lower maintenance and operator supervision required for ACE Separator™ operation and the capability to use ACE Separator™ treated water in closed-loop, zero-discharge applications adds to its attractiveness. Successful commercialization of the technology requires further research to significantly improve aluminum dissolution efficiency. If the ACE Separator™ can be engineered to regularly generate sufficiently high aluminum dissolution concentrations, the technology may be applicable to industrial effluent treatment trains, as well as for some Superfund site remediation activities.

Incorporation of an automated process control system based on influent conductivity and solids loading, or on the discharge solution's supernate turbidity, needs to be engineered. An automated system for addition of replacement aluminum pellets may be justified, although the frequency of pellet addition should be predictable after an initial period of operation. The capital cost for a standard ACE Separator™ with nominal throughput capacity of 50 gpm is estimated at $80,000 and for a 250-gpm unit, $300,000.

Conclusions

ACE offers a promising alternative for treating waste streams containing clays, certain metal constituents, and other soluble pollutants. As an alternative to chemical conditioning, ACE Technology agglomerates the particles without adding any extraneous soluble species (i.e., SO_4^{2-}); the sludge it produces has a lower bound-water content that will filter more rapidly and has a lower susceptibility to filter shear of the coagulated particulates and emulsion droplets.

As a result of the pilot-scale efforts, we compared the effectiveness of ACE Separator™ treatment, alum addition, and polymer coagulation. Conclusions drawn from this comparison for various contaminant parameters were:

- TSS: ACE Separator™ treatment and the polymer treatment yielded equivalent results for the reduction of TSS in the treated supernates. TSS values for alum treatment were four to five times greater than those for ACE Separator™ treatment or polymer treatment.
- COD: ACE Separator™ treatment resulted in the highest COD reductions of the three methods. Removal efficiency for COD was from two to four times higher than removal efficiency for either alum treatment or polymer treatment.
- Lead: ACE Separator™ treatment achieved approximately 66% removal of lead in the high metals runs, whereas polymer treatment showed a slightly higher removal (71%). Because some difficulties were experienced with the alum treatment, these test results were invalidated. Further ACE Separator™ treatments of slurries with low concentrations of metals yielded the highest lead removal (96%).
- Copper: Copper in the supernate achieved dramatic removal by electrocoagulation in both the high (90% reduction) and low (99% reduction) metals concentration experiments. In the former, however, polymer and alum addition achieved greater removal (approximately 100% reduction).
- Chromium: ACE Separator™ treat-ment resulted in good removal for total chromium (87% and 94% reductions for the high and low concentrations). Alum and polymer addition accomplished similar removal.
- Cadmium: Cadmium levels in the supernates dropped as a result of ACE Separator™ treatment: 14% in the high metals runs and 99% in the low metals tests. The inconsistency between these two sets of experiments, as well as the high concentrations remaining in the supernates and filtrates, raises questions about the accuracy of experimental results involving high concentrations of metals. For the low metals tests, the cadmium concentrations in both ACE Separator™ filtrates were much lower than were the concentrations for either alum or polymer treatment.

The following generalization on the effectiveness of the ACE treatment can be made:

- ACE Separator™ treatment consistently reduced the TS and TSS loadings to an equivalent degree and to approximately one-quarter the level achieved through alum addition; and
- Better reductions in soluble metal concentrations are achieved with electrocoagulation treatment than with alum treatment.

In summary, ACE offers a promising technically simple method for achieving solids-liquid separations in aqueous-based waste streams. The majority of the nontoxic, aluminum ionic species introduced will be removed in the coagulated solids phase. The ACE Technology may be particularly suitable for zero-discharge applications in which the addition of chemicals and the buildup of residual concentrations (dissolved solids) would adversely affect effluent quality or inhibit effluent reuse. Other potential applications of the ACE Separator™ include: (1) remediation of groundwater and leachates (metals, COD/BOD removal), (2) enhancement of clay separation from aqueous suspensions/emulsions resulting from soil-washing operations, (3) breakage of oil/water emulsions produced in the pumping of hydrocarbon contaminated groundwater, and (4) removal of TSS from stormwater runoff. Possible industrial applications are fine-grained product recovery (pigments, PVC) and extraction of TSS from waste streams that contribute to high BOD and COD loadings.

☆U.S. GOVERNMENT PRINTING OFFICE: 1993 - 750-071/80064

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Details of the completed SITE Emerging Technology project are given in a journal article published in Air and Waste, Vol. 43, No. 5, p. 784-789, May 1993. The journal article entitled "Alternating Current Electrocoagulation for Superfund Site Remediation," (Order No. PB93-205 144; Cost: $12.50, subject to change) is also available from:

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