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Electroflotation From the Double Layer to Troubled Waters†

Klaus Müller

1. INTRODUCTION

Among technologies with an electrochemical basis, electroflotation appears certain to find expanding applications in the 21st century. Electroflotation (EF) is a separation technology for aqueous fluids containing suspended matter, designed to produce water pure enough to discharge and residues concentrated enough for further workup. After additional compatible processes, the water is suitable for recycle, while the residues may, depending on the particular application, constitute a raw material for food, feed, and fuels, allow mineral and metal values to be extracted, and/or simply become disposable waste.

Electroflotation has a long history of successful short-term applications as well as of failures. Most of the problems have now been solved on a technical scale. The reference list of long-term operations is growing steadily, but little notice has been taken in the recent electrochemical literature. It is a different matter, of course, to decide whether EF, at a given time and in a given situation, is an economically feasible technology. For some of the environmentally most troublesome effluent situations, the answer is "yes" now. For more of them, and for a great many recycling and extraction problems in the next century, the answer is "very likely so."

2. PRINCIPLES

2.1. The EF Blackbox

Electroflotation is an electrochemical version of flotation. It differs from flotation mainly in the mechanism of bubble generation. The bubbles are generated by electrolysis, usually of the substrate stream itself or of an auxiliary electrolyte stream. The bubbles produced at electrodes are very fine, are uniform, and rise very slowly, and bubble generation produces

† *Troubled waters*: A situation or condition of disorder or confusion (Webster's Third New International Dictionary).

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little undesired convection (though probably more than has been thought for a long time, according to recent Soviet work[1]).

Flotation processes separate suspended matter from fluids. In EF, this occurs without a size classification. The gas bubbles become attached to the suspended particles, and these are lifted to the top of the fluid, where they are collected as a sludge; hence, the suspended matter and the fluid can be used or disposed of separately. For a separation of species originally present as true solutes, precipitation or coprecipitation must precede flotation. For the separation of colloidal matter, coagulation/flocculation or adsorption must precede flotation.

EF equipment can be sketched as shown in Fig. 1. Into the EF tank go:

- a stream of the fluid to be treated (e.g., effluent, fruit juice, or a mineral slurry, part or all of which may have been pretreated),
- streams of fluid containing chemicals aiding flotation (the point of entry actually is upstream from the tank),
- dc power to the electrodes.

Out of the EF tank come:

- a purified fluid stream, usually from the bottom,
- concentrated residue (sludge), usually from the top,
- the electrolysis gases (some dissolved in the off-fluid, some contained in the sludge, and some directly vented).

Floor-space requirements for the EF tank depend on throughput; they will be between square meters and tens of square meters. Tank height is on the order of 1 m. Throughputs of operating plants are cubic meters to hundreds of cubic meters per day. This is much below the scale of (nonelectro) flotation equipment found in the minerals industry. The EF units are relatively quiet in their operation.

More technical background will be provided in the last part of the present section and in the sections on applications that follow.

2.2. The Double-Layer Connection

Legion are the examples where fundamental inquiries into the structure and properties of the electrical double layer at interfaces have been justified by the importance of the results, in terms of practical applications or their understanding. Colloid science constitutes the area where the loop between theory and practice has been closed most successfully. A similar claim cannot be made in the case of EF. So where is the double-layer connection?

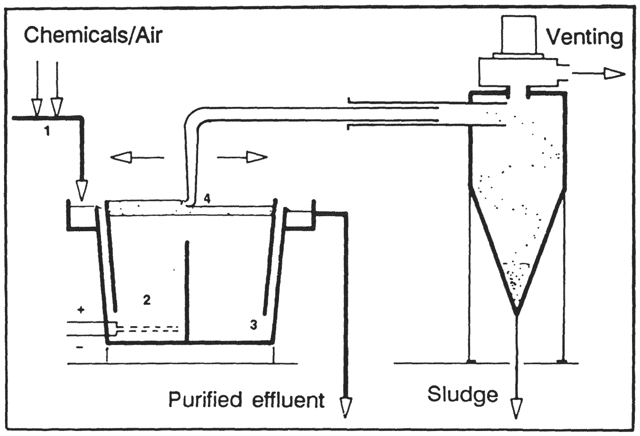

FIGURE 1. Schematic of electroflotation unit. Effluent enters from the left, after appropriate addition of chemicals. Flotation and separation occur in the central unit holding electrodes (+ and −). Sludge collects at the top from where it is removed; it then undergoes degassing (venting) and further dehydration. Purified effluent leaves the EF unit. (Kindly provided by Dr. E. Baer.[36])

It is somewhat indirect. It will not suffice to say that all interfaces are charged, though this is a correct opening statement.

2.2.1. The Suspended Matter

The substrate in EF is a suspension of finely divided matter (liquid and/or solid; e.g., oil emulsions). In such matter, the charge *may* be a highly important factor in stability (before the treatment, at the stage of the "problem") and destabilization (during pretreatment; emulsions and similar, stable colloidal systems must be broken prior to separation by EF). In a technical report on the treatment of oil-sand production recycle water from the University of Alberta,[(2)] which reads like a dissertation on the subject, the double layer (around the particles) has been discussed as the starting point of an apparently successful practical evaluation of EF.

2.2.2. The Bubbles

The "motor" in any flotation process (not merely in EF) is the gas bubbles. They, too, are charged, and their charge, too, will be more important, the finer they are. The claim is made that, when the bubbles are generated electrolytically, the parent electrode influences their charge; also, electrolytic bubbles are finer (how much so will be a question of solution pH and electrode polarity). Unfortunately, bubbles have been much less popular than mercury drops in double-layer studies. Moreover, though it may be attractive to think of the elegant attraction of positively charged bubbles to negatively charged particles, flotation actually has an optimum at zero zeta potentials of the bubbles and is most efficient when the particles are at their point of coagulation/flocculation.

2.2.3. Electroflotation and the Hamaker Constant

Not many papers can be consulted which provide information concerning the fine details of the kinetics and mechanism of individual EF steps. Panov and Kravchenko[(3)] discussed the inevitable supersaturation which must exist in the solution (because of the Kelvin equation) when very small bubbles are present in equilibrium. Kul'skii *et al.*[(4)] discussed the effect of the degree of contaminant dispersion on coagulant and energy requirements. Fukui and Yuu studied flotation kinetics with model dispersions to see the effect of bubble diameter and bubble charge[(5,6)]; they also reported that several companies in Japan have succeeded in treating effluents by EF. Fukui and Yuu's treatment considers the effect of Hamaker constants and zeta potentials as the important factors in particle collection by charged bubbles.

Among relevant papers in colloid chemistry, Watanabe's[(7)] is a fairly recent review of the oil/water interface; adsorption and the interaction between model drops were considered. Elsewhere,[(8)] particle interactions have been discussed in the context of flotation in terms of surface potential and surface charge of the particles.

Bubble properties have been studied for a long time. Small bubble sizes are found for the cathodic gas in alkaline solutions, but for the anodic gas in acidic solutions[(9)]; bubble size also is a function of electrode diameter (40-μm bubbles were produced at 0.2-mm-diameter wire,† 130-μm bubbles at 1.5-mm wire, and there is a sharp size distribution maximum),[(10)] temperature and electrode material have influence on bubble size, and an optimum current density of 20 to 30 mA/cm^2 was reported.[(11)] Typical bubble sizes in EF are between 20 and 70 μm. Bubble rise velocities decrease with increasing electrolyte concentration and with

† In a recent example,[(119)] optimum EF treatment of meat processing wastewater was achieved with a wire diameter of 0.2–0.5 mm, mesh grid size of 2.5–5.0 mm, and an inclination of the electrodes of 30–45° to the horizontal.

surfactant addition (this was found for relatively large bubbles[12]). Clean bubbles rise faster (there is an analogy to the fall of mercury drops: the clean interfaces are mobile, which is responsible for the higher speed), while bubbles rigidified with surfactant rise more slowly.[13] Bubble charge was found to be positive at $pH < 2$ and negative at $pH > 3$; that is, the bubbles have an isoelectric point or point of zero charge at a pH of 2 to 3,[9] which was confirmed quantitatively by bubble electrophoresis.[13] Double-layer structure appears to be governed by negative adsorption of ions (e.g., H^+ or OH^-) at the water/gas interface. In bubble growth, there is an induction time (supersaturation must be reached), a period where growth is sustained by diffusion, and finally a period where growth is sustained faradaically.[9]

In the area of flotation kinetic studies, some more papers are available which take the same direction as Fukui and Yuu's. It was noticed that a finite time is required for bubble and particle to become permanently joined.[14] Charge on the particles and bubbles may be detrimental, and the molecular component of the forces may be preponderant; maximum floatability was found to occur at the isoelectric point.[15] There is a hydrodynamic factor, since liquid streaming around the bubbles is important in the stage preceding attachment; the Reynolds number in surfactant-free systems (but this would appear to be a rather exceptional case!) should be between 1 and 40. Microbubbles are likely to get attached to hydrophobic sites of the floc, and high shear should be avoided.[16] The benefits of using small bubbles seem to be large: flotation rates rise with the inverse third power of bubble radius.[17,18] In model systems, it was found that minute particles first will become attached to, or deposit on, the surface of small bubbles, and such aggregates then are floated by larger gas bubbles.[19] This mechanism is helped by the fact that the microbubbles actually are stabilized by the sheaths of colloidal particles which become attached.[19]

2.2.4. From the Double Layer to Troubled Waters

It must be doubted, despite the theoretical work cited in Section 2.2.3, that double-layer theory has as yet been a quantitative help in putting EF processes to work. Its relevance and value as a guide is evident, and anybody with a background in double-layer structure and/or colloid science should enjoy the introduction to EF afforded by this background. It is gratifying to see that a process in which double-layer properties (but not merely the electrostatic ones) play a basic role can convert some of the most troublesome effluents back to usable water.

2.3. Early Hopes and Failures

To look back is not the purpose of this contribution. May it suffice, therefore, to say that the history and applications of EF have been reviewed, for example, by Kuhn,[20] that many companies and workers have been involved in the past, and that spectacular separation and cleanup operations have been described (from hog farm effluents to diamond fines), yet it must be suspected that many initially successful operations did not continue forever. The reasons are:

(i) technical complications: many of the early engineers in the field put the steps of flocculant generation, emulsion breaking, and flocculation right into the EF tank's electrode region, which may have brought an untractable situation in the long run;

(ii) technical difficulties: viz., formation of undesirable deposits on the electrodes and undesirable corrosion of the electrodes; and

(iii) competition and price: a chicken farm might not be able to support the bill for electric power† and advanced electrode designs, a hog farm's effluent volume and

† However, it has been reported that a poultry waste digester could produce biogas to the extent of about 10 W h/day per caged layer.[120]

its contaminant load probably are too high, dissolved-air flotation (or an altogether different method) may have provided a solution at a lower price or, lastly, environmental concerns may not yet have motivated a cleanup at all.

2.4. Breakthrough to a Viable Technology

The following is a list of requirements which must be met for fluid treatment by EF.

- The fluid must be sufficiently conductive for economy of the electrolysis process producing the gas; if it is not, electrolyte must be added (e.g., industrial waste brines or seawater), and it has been suggested that a special electrolyte loop be created only around the electrodes.
- The suspended matter in the fluid must be floatable; this may require prior steps such as emulsion breaking/coagulation, aggregation/flocculation, or the attachment to carrier particles (hydroxide flocs) as well as surface modification of the minute particles by special chemicals. Also, this requirement implies limitations with respect to the specific gravity and number density (concentration) of the suspended particles.
- There may be optimization requirements such as using one or both electrolysis gases, simultaneously producing disinfectant (anodically from chloride ions), or using cathodic pH variation and anodic dissolution to produce hydroxide particles, but all this must occur without interference with the EF lifting act. Also, any chemicals added should not contribute to cleanup problems, and they should preferably be recycled (such as iron and aluminum for floc).

What has persistently caused trouble in long-term operation was incrustation of the electrodes, particularly the cathodes. The phenomenon is not perfectly understood; precipitation by pH variation, electrophoretic deposition, or cathodic (and anodic) electrodeposition may be involved. Mechanical cleaning of the electrodes not only is cumbersome, disruptive, and expensive, but also actually very difficult. A good solution to this problem, polarity change of the electrodes during operation, which in itself will not upset the EF process, was unsuccessful because of excessive corrosion until the quite recent development of stable, nonconsumable electrodes which will operate without corrosion and passivation as anode *and* as cathode, in alternation. This must be regarded as a true breakthrough (no less so than the success of the stable metal-oxide anodes in chloralkali electrolysis).

The structure of these electrodes has been disclosed as being Ti/TiO_{2-x}, Pt[21]; they are available from Heraeus Hanau, Germany, and their different applications (in addition to electroflotation) have been described. Important points are their high surface area and highly open design (see Fig. 2). Among other companies supplying platinized titanium electrodes, Engelhard can be mentioned.

2.5. Where to Look

While practical applications recently have multiplied (see below), other strong technologies for separations and water treatment are available or under development, and in some recent symposia about water treatments and separation technologies,[22,23] EF was not a central topic. Literature reviews preceding the "electrode breakthrough" (see above) should, of course, be digested "with a grain of salt." One speculates that investment requirements for the process have become somewhat higher than figures provided occasionally in the more distant past, on account of superior electrode design, though operating costs should be relatively lower now. With this in mind, the interested reader can go back and consult earlier reviews and book chapters.[24–30] Romanov has restated a great many of the salient points

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