9 Treatment of Metal-Bearing Effluents: Removal and Recovery

Ghinwa M. Naja and Bohumil Volesky

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9.1 PHYSICO-CHEMICAL TREATMENT

9.1.1 Chemical Precipitation

The most common method for heavy metal removal from wastewater is chemical precipitation. As shown in Figure 9.1, the basic treatment process for precipitating heavy metals includes pretreatment, pH adjustment, flocculation/clarification, sludge thickening, sludge dewatering, and effluent polishing [1].

The general principle of heavy metal removal by chemical precipitation is based on the low solubility of heavy metal hydroxides. The treatment reduces the heavy metal content of the water dramatically, thus the residual concentrations of heavy metals in the overflow from the settling tank are usually below the environmental limits. Furthermore, the process can handle relatively high flow rates of wastewater containing high concentrations of heavy metals, and so it is suitable for the treatment of many industrial and mining effluents. However, the efficiency of the treatment hinges on the rates of formation and of settling of the solid metal hydroxides. The fact that these rates are usually low in water with low metal content leads to an increase in the consumption of lime and/or caustic soda in the process, and to the design of large mixing and settling tanks. Furthermore, the treatment generates toxic sludge that has to be dewatered, stabilized, and disposed of.

Three theories have been put forward to explain the effects and efficiency of chemical precipitation. The first theory uses the fact that heavy metal salts when treated with alkaline substances,

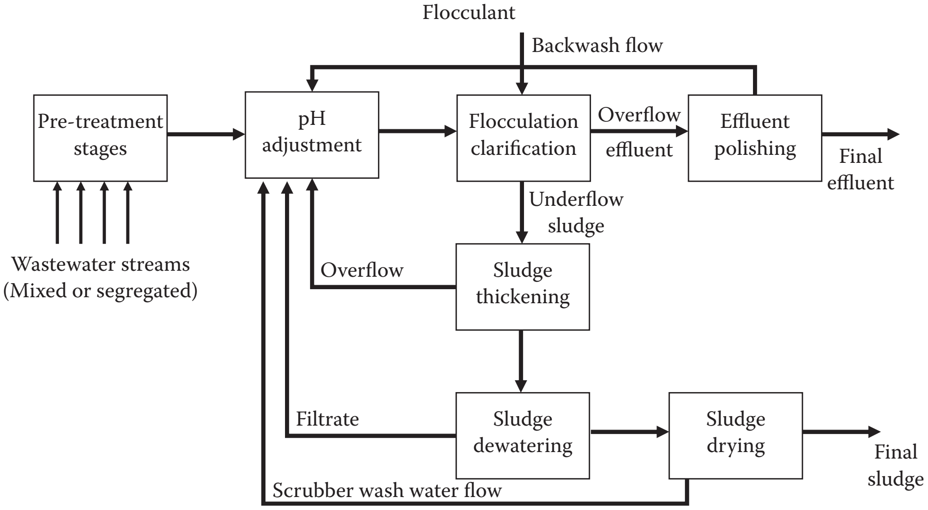

FIGURE 9.1 Basic waste treatment process for heavy metals.

form heavy voluminous precipitates that carry down colloidal suspensions by means of mechanical entrapment. Salts of iron, aluminum, and zinc fall into this category. The second theory is based on electronic principles. It has been demonstrated that colloidal particles possess an electric charge. Since these charges are alike, the particles repel each other and thus tend to remain in suspension. If a colloidal particle with an opposite charge is added, the charges neutralize and settling of the particles is affected. This explains the efficiency of the multivalent ions and why ferric salt is more efficient than ferrous salts. Clay suspensions are also claimed to exert a charge-neutralizing effect. The third theory pertains to a physical behavior. Insoluble substances that have a large particle surface area can effectively sorb colloids. They can also act as nuclei for the initiation of precipitation. Activated charcoal is a material with this type of action. Of the three theories mentioned above, the second one is generally predominantly accepted.

9.1.1.1 Pretreatment

Prior to precipitation, the wastewater will be subjected to a pretreatment stage. Pretreatment is used to remove materials such as grease and scum before sedimentation to improve process feasibility. Common pretreatment stages include oil removal and chromate reduction (Cr(VI) to Cr(III)).

If significant levels of oil are present in metal-bearing wastewater streams, the oil must be removed before clarification to prevent interference with the settling of the precipitated solids. The oil is usually removed by skimming, and emulsified oil can be removed by ultrafiltration. Chromium will only precipitate in the trivalent form and thus it must be reduced from its hexavalent form prior to precipitation. Hexavalent chromium reduction is achieved at low pH levels (~2–3) with a reducing agent—usually sodium metabisulfite. Owing to the low pH level involved, chromium-bearing wastewater is usually segregated for pretreatment before being mixed with other metal-bearing wastewater streams [2].

9.1.1.2 pH Adjustment

The precipitation of metals occurs at various pH levels depending on a number of factors. For wastewater streams that contain various heavy metals, the pH level for precipitation must be carefully chosen so that all of the metals have an acceptable level of insolubility. If this is not possible, the stream will have to be segregated to treat the particular component metal at an appropriate pH level [3]. Typical minimum pH values for precipitation are given in Table 9.1, depending on the solubility product K_{sp} of the metal hydroxide [4]. To precipitate metals in the hydroxide form, caustic soda and

TABLE 9.1
Minimum pH Values for Complete Precipitation of Metal Ions as Hydroxide

Metal	Sn^{2+}	Fe^{3+}	Al^{3+}	Pb^{2+}	Cu^{2+}	Zn^{2+}	Ni^{2+}	Fe^{2+}	Co^{2+}	Mn^{2+}
pH	4.2	4.3	5.2	6.3	7.2	8.4	9.3	9.5	9.7	10.6

Source: US Environmental Protection Agency (US EPA). Processes, procedures and methods to control pollution from mining Activities. US EPA # 430/9-73-011, 1973.

lime are frequently used for pH adjustment. In large wastewater treatment systems, lime is preferred due to its lower cost, whereas in small wastewater treatment systems, caustic soda is used due to ease of handling. In the case where fluoride or phosphate removal from the wastewater is required, lime is used for pH adjustment since it will generally cause precipitation of the fluorides and the phosphates. Precipitate particle size (and filterability) appears to be greater when lime is used. The use of lime or caustic soda seems to have no great effect on the rate of sedimentation, but the volume of sludge will be twice as great when using lime as when using caustic [5].

9.1.1.3 Coagulation/Flocculation/Clarification

As the metal hydroxides come out of solution due to pH adjustment, chemicals are often added to promote coagulation and flocculation. The inorganic coagulants are often trivalent cations to neutralize the negative charge of the colloids. The higher the valency, the more effective the coagulating action will be (Schultz–Hardy theory: a trivalent ion is ten times more effective than a divalent ion). When choosing a coagulant, its harmlessness and its cost must be taken into account. Thus, trivalent iron or aluminum salts have been and continue to be widely used in all water coagulation treatments. Organic coagulants may also be used. These are cationic polyelectrolytes that directly neutralize the negative colloids. Inorganic polymers (activated silica) and natural polymers (starches, alginate) were the first to be used as common flocculants. The appearance of the widely varying synthetic polymers has changed flocculation results considerably. Of chief importance is the timing of the introduction of the coagulant and that of the flocculant. In fact, a flocculant usually does not take effect until the coagulation stage is over. The use of synthetic flocculants often results in a minimum amount of sludge. Combined with modern separation techniques, this can lead to the production of very dense sludge that can be directly treated in a dewatering unit.

High-molecular-weight polymers are fed to the neutralized waste as it enters the clarifier at a dosage of 10–100 ppm [5]. Exact flocculant dosage is usually determined by individual bench tests. Prior to the clarification stage, flash mixing and flocculating chambers allow the flocculant to be well mixed into the wastewater and provide gentle particle contact to aid the formation of larger, heavier particles, which will settle well in the clarification stage.

The clarification stage involves the removal of the solids (the flocs) from the wastewater stream. This is typically a gravity settling process that occurs in a sedimentation tank or in an inclined plate clarifier, also called a Lamella clarifier. Under proper conditions, precipitated solids can be concentrated about 10:1 in a clarifier. Clarifier performance is largely a function of the settling surface that increases by utilization of the Lamella clarifier. In summary, a clarifier has to usually perform three different functions in order to do its task well [1]. The settling tank thus must

- Provide for effective removal of suspended solids from the effluent
- Have an adequate sludge removal capacity
- Thicken the sludge satisfactorily.

Any failure in one of these functions will impair the performance of the settler and, if serious, destroys the effectiveness of the process almost completely. A poor design results in the propagation of the problem to successive units within the plant, and inevitably in a decrease in the overall performance of the treatment.

9.1.1.4 Solid–Liquid Separation

If further reduction in the level of suspended solids is required, the effluent can be polished. Filtration using backwash sand in-depth filters is the most popular method for suspended solids removal in the polishing stage. The overflow from the settler/clarifier enters the filtration process. After passing downward through the granular medium, it can be discharged. During backwashing, wash water passing upward through the filter (fluidizing the sand filter medium) carries out the impurities that accumulated in the filter bed. A continuous backwash sand filter can provide continuous streams of polished effluent and reject flow so that the filter never needs to be shut down for backwashing. The reject flow would be returned to the front end of the treatment system for further processing. The effluent from this type of sand filter is usually quite clear, containing only 3–5 ppm of total suspended solids [6].

Apart from gravity settling, membrane filtration processes offers another approach to concentrating the solids from the wastewater stream and producing clear effluent. Ultrafiltration could be quoted as an example. It is a physical membrane separation process whereby the membrane acts as a barrier to precipitate particles, and prevent their passage into the discharge stream. No flocculants are needed and the total suspended solids in the effluent are essentially zero. Thus tighter effluent limits are met and even high flow rates can nowadays be handled [7]. Ultrafiltration systems are based on the cross-flow membrane technology. A bundle of parallel hollow fiber membranes is sealed into a shell to form a cartridge. Each cartridge has a process inlet, outlet, and a pair of permeate outlets. Inside each fiber, waste is separated at the membrane surface. Cleaned effluent passes through the membrane, whereas contaminants are rejected and exit at the opposite end. Turbulent flow across the membrane surface reduces waste build-up and minimizes cleaning.

9.1.1.5 Sludge Thickening

The flocculation/clarification stage is usually followed by the sludge-thickening stage. A sludge thickener is typically a conical bottom tank that receives the underflow from the clarifier and provides storage where further gravity settling of solids can take place. The sludge concentrated at the bottom of the tank contains about 4–6% solids [5]. The advantage of operating with a high solids content sludge is that it generally improves the operation and performance of the dewatering equipment.

9.1.1.6 Sludge Dewatering

Dewatering of the concentrated sludge can be accomplished using a wide variety of equipments such as centrifuges, rotary vacuum filters, belt presses, and filter presses [8]. Rotary vacuum filters produce a relatively dry cake (20–25% solids) and can operate continuously so that they are suitable for applications involving large volumes of sludge. For most industrial applications, filter presses (plate and frame pressure filters) are the most economical method of producing a dry cake (20–30% solids). Filter presses have wide applicability and are probably the most common type of dewatering equipment in use [5]; however, they do not operate on a continuous-flow basis. A filter press consists of a series of plates lined with polypropylene filter cloths. The plates form chambers into which the sludge is pumped. The solids are retained by the filter media, whereas the filtrate flows through the porous filter cloths. The filtrate flow is discharged from the press to the front end of the treatment process (prior to the clarification stage). As the filter cycle progresses, the chambers become completely full of solids and at this point, no more sludge can be pumped into the press. The press must then be opened and the dry cakes are discharged. Therefore, the term “press” is a misnomer because no mechanical squeeze is involved. It should be noted that only the thickening of neutralized metal hydrates by means of a clarifier and subsequent dewatering of sludge has been discussed to this point. The neutralized waste can also be pressure filtered directly, depending on its concentration (about 300–500 ppm of suspended solids).

9.1.1.7 Sludge Disposal

With increased production of industrial wastes, sludge management is becoming increasingly important [9]. There exist various methods of disposing sludge (landfill 25%, ocean dumping 10%, incineration 40%, and land application 25%). Metal-bearing sludges are difficult to handle and, due to their toxicity, their final disposal is often troublesome and expensive. If incorrectly disposed of, these sludges could be a potential source of pollution of surface and ground waters. There appears to be little problem concerning the incineration of waste sludges with respect to heavy metals, but this depends on where and how the pollutant is released. Ocean dumping is being less used compared to land applications and sludge landfilling. In determining the sludge disposal site, many factors need to be considered, such as type of soils, ground water table, hydrology, composition, and pH of the sludge. With a sludge pH of less than 6.5, the potential for release of cadmium, chromium, lead, mercury, and selenium increases. Suitable disposal sites are areas where natural (clay, rock) or artificial means (plastic liner) can prevent excessive amounts of leachate from getting into the ground water. Where these conditions do not exist, it may be necessary to install a collection system at the bottom of the pond so that leachate can be collected and piped to a treatment system for removal of soluble metals salts. The US EPA has suggested limiting sludge land application as a function of specific metal content and soil cation exchange capacity [10]. Chemical treatments have been developed to reduce the leaching possibilities of metal-bearing sludges and may be used in conjunction with a land fill program to further minimize potential leachate contamination. One other solution could be to remove metals from these sludges (Section 9.1.4).

9.1.2 TREATMENT METHODS

Chemical precipitation of metal may be accomplished in either batch (Figure 9.2) or continuous treatment systems (Figure 9.3). Batch treatment is usually preferred when the volumes to be treated are small, or where the waste may be variable from day to day and require modification of the treatment as characteristics change [1].

9.1.2.1 Batch Treatment

Batch treatment systems can be economically designed for flows as high as 50,000 gpd. A batch system is usually designed with two tanks, each one of sufficient volume to handle the waste generated in a specific time. When one tank is full, a mixer is used to provide a homogeneous mixture, and a sample is taken and analyzed to determine the amount of metal contaminants present.

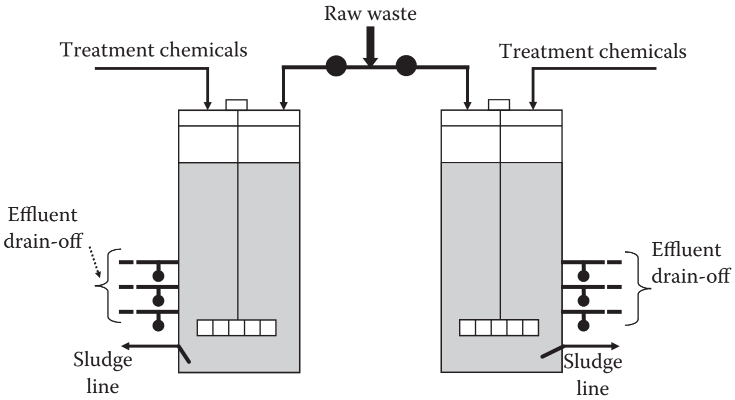

FIGURE 9.2 Typical batch treatment system.

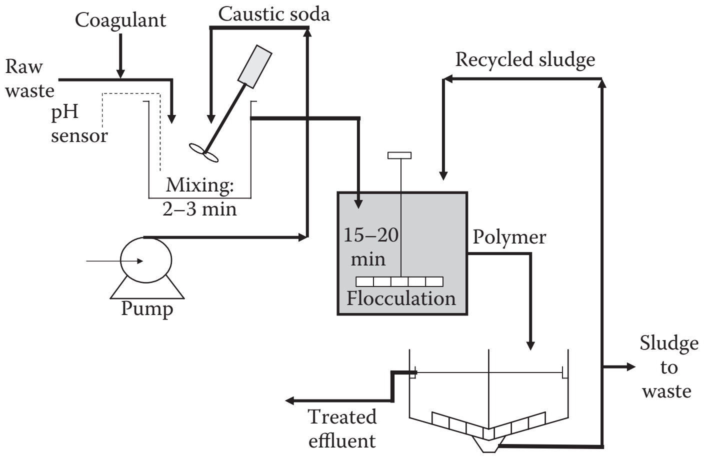

FIGURE 9.3 Typical continuous-treatment system for heavy metals.

Chemical addition, based on the metal contaminants present and pH of the waste, is then calculated and the required amount of chemicals added. The tank contents are then mixed, using pH for controlling purposes and for metal removal, and allowed to settle for 2–4 h.

When treatment is complete, a second sample can be taken and analyzed to ensure that all contaminants have been removed. If, for any reason, contaminants are still present, treatment can be repeated or alternative treatment applied. When the operator is satisfied, that the treated waste is suitable for discharge, the clear liquor is decanted. The settled sludge is drawn off periodically for disposal. The advantages of a batch treatment system are that nothing is discharged from the plant until the operator is satisfied that it meets effluent requirements. The system is also simple in its design and is easy to operate (Figure 9.2).

9.1.2.2 Continuous Treatment

When wastewater characteristics are uniform or when volumes are large, a continuous treatment system is applicable. A usual continuous-flow treatment system has an equalization tank of several hours to a day of detention time to even out any fluctuations in the wastewater characteristics and provide a uniform feed to the treatment system.

The first process step is the adjustment of the pH by addition of acid or alkali to the proper level of optimum precipitation. This chemical addition is controlled by a pH probe in the reaction tank, which activates the speed control of the chemicals feed pump. A polymer is usually added to aid coagulation. Reaction times are in the range of 15–60 min.

The waste stream then flows to a sedimentation basin where the metal precipitate settles out of solution, leaving a clear treated overflow for discharge to the receiving water body (Figure 9.3).

9.1.2.3 Sludge Recirculation

Recirculation of precipitated sludge to be mixed with the raw waste at the time of chemical addition can have beneficial effects. The presence of precipitated particles provides a seed for the newly formed precipitate to agglomerate. In a batch treatment, the settled sludge is collected at the bottom of the tank. When a new batch is put in the tank, the mixer is turned on to resuspend the sludge and mix it with the tank contents.

In continuous treatment systems, the sludge can be recycled either externally to the clarifier or internally within the clarifier. With external recirculation, the sludge is pumped out of the sludge hopper in the clarifier and introduced to the raw feed in the chemical mixing tanks. With internal recirculation, the clarifier is designed with an internal mixer and baffles that provide recirculation within the clarifier.

9.1.3 APPLICATIONS

9.1.3.1 Zinc

The precipitation process most frequently involves adjustment of pH with either lime or caustic to achieve alkaline conditions, and precipitation of zinc hydroxide. Lime addition has been the widely accepted method for pH adjustment, despite the concurrent precipitation of calcium sulfate at elevated sulfate concentrations in some waters. The precipitation of calcium sulfate along with zinc hydroxide increases the total amount of sludge to be disposed of. Table 9.2 summarizes some results of zinc precipitation to its hydroxide. These values reflect a wide range of industrial systems; the treatment is usually not just for zinc removal alone. In cases where cyanide or chromate is also present in the waste, as frequently occurs in zinc and brass plating, cyanide removal and chromate reduction must precede metal hydroxide precipitation. Settling efficiency affects effluent concentration, as it can be seen in Table 9.2 by improvements in effluent zinc levels resulting from filtration of settled effluent. Incomplete cyanide treatment will increase effluent zinc levels, due to complexation, as will improper control of the treatment process pH.

9.1.3.2 Lead

In the precipitation process, lead is normally precipitated in the form of carbonate ($PbCO_3$) or hydroxide $Pb(OH)_2$. The lead form precipitated depends on the amount of carbonate in or added to the wastewater, and the treatment pH. Initial acidic wastes are typically low in carbonate, and precipitation treatment of these waters would normally yield lead hydroxide unless supplemental carbonate was added. Lead carbonate precipitate is more crystalline than lead hydroxide, resulting in desirable settling and sludge dewatering characteristics. A large excess of carbonate, or treatment above pH 9.0, may yield less effective precipitation, however. Optimum pH range for lead carbonate precipitation is between 7.5 and 9.0.

In forming insoluble lead hydroxide, lime is the treatment chemical of choice, although caustic has also been used. The results with caustic or lime treatment are equivalent but there is an interference with lead hydroxide precipitation as calcium ion concentration increases.

TABLE 9.2
Summary of Hydroxide Precipitation Treatment Results for Zinc in Wastewaters

	Zinc Concentration (mg L^{-1})		
Industrial Source	**Initial Final**	**Final**	**Comments**
Zinc plating	—	0.2–0.5	pH 8.7–9.3
General plating	4.1–120	0.39–2.9	pH 7.5–10.5
Vulcanized fiber	100–300	1.0	pH 8.5–9.5
Brass wire mill	36–374	0.08–1.60	Integrated treatment for copper recovery
Tableware plant	16.1	0.02–0.23	Sand filtration
Viscose rayon	20–120	0.88–5	pH 5
Metal fabrication	—	0.5–1.2	Sedimentation
	—	0.1–0.5	Sand filtration
Blast furnace gas scrubber water	50	0.2	pH 8.8
Zinc smelter	744–1500	26–50	
Ferroalloy wastes	3–89	0.29–7.9	

9.1.4 Metal Recovery from Sludges

The settled sludge from a clarification basin is frequently in the range of 1–2% solids. Hydroxide precipitation of the metals produces sludge that is usually gelatinous in character, thereby increasing the difficulty of dewatering. Lime will produce considerably greater quantity of sludge than caustic, but that kind of sludge is easier to dewater. Similar to the case with wastewater sludges, the composition of these water treatment sludges varies from plant to plant, necessitating individual attention [9]. Some sludge compositions for North American plants are available in Table 9.3.

Metal recovery from sludges has been studied [11]. Digesting the sludge in an acid medium, neutralization and electrolytic recovery have been investigated [12,13]. The cost estimate for recovery of copper, nickel, and chromium in a small plant was \$13.25 kg^{-1}, which was quite high compared to the current market prices. However, since these metal values are steadily increasing, one approach is to stockpile these metal-bearing sludges, either separately or in a regional disposal site, so that they are available for economical metal recovery in the future.

Nevertheless, digestion of the sludge can be done biologically. The further paragraphs will compare acid and microbial leaching for metal removal from municipal sludge.

A number of chemical methods for toxic metal solubilization from sludges have been studied [14,15]: ion exchange [16,17], utilization of chelating agents (EDTA and similar) [18–20], aerobic digestion coupled with or without hydrochloric acid [21–23], or oxidative acid hydrolysis [24]. The relatively high operating costs and sometimes insufficient yield of metal solubilization are obstacles in their practical applicability. The acid leaching (H_2SO_4, HCl, HNO_3, CH_3COOH) with or without heating are the processes that have been given more attention. The requirement of large amounts of acid to adjust pH and large amounts of alkali for residual sludge neutralization after the leaching

TABLE 9.3
Metal Composition in the Sludges and their Recommended Levels

	Composition (mg Kg^{-1} of Dry Sludge)							
	Al	**Cd**	**Cr**	**Cu**	**Mn**	**Ni**	**Pb**	**Zn**
Plant #1[a]	27,640	5.0	87	215	933	28	110	419
Plant #1[b]	26,320	2.6	66	200	1053	42	234	392
Plant #2[a]	43,630	9.2	401	1070	445	141	278	413
Plant #2[b]	22,120	10.0	1719	1827	395	177	336	596
Plant #3[a]	74,097	1.4	50	178	323	17	23	359
Plant #3[b]	77,734	0.7	26	147	365	13	15	285
Plant #4[a]	30,907	4.5	124	737	4613	30	177	379
Plant #4[b]	18,589	4.0	87	625	5696	26	129	343
Plant #5[a]	32,484	2.3	99	1211	2914	142	266	181
Plant #5[b]	18,039	1.9	97	1282	2450	151	225	151
Plant #6[a]	28,786	0.8	349	1017	1458	50	43	1430
Plant #6[b]	27,430	7.7	321	603	1519	45	118	1205
Plant #7[c]	21,705	11.2	116	3689	166	23	447	1024
Plant #8[c]	19,340	7.9	98	2279	444	13	646	646
Plant #9[a]	13,520	2.0	155	391	418	222	106	1456
Plant #6[c]	27,009	3.7	288	462	1013	274	155	1926
Recommended levels	—	15	1,000	1000	1500	180	500	2500

[a] Secondary activated sludge.
[b] Aerobically digested sludge.
[c] Anaerobically digested sludge.

makes these processes unattractive from a practical standpoint. Consequently, interests have also focused on developing new microbiological methods. Two microbial leaching processes have been studied to remove toxic metals from sewage sludge. The bioleaching process with iron-oxidizing bacteria requires a lowering of the initial sludge pH to 4.0 and the addition of ferrous sulfate as a substrate, whereas the microbial leaching process with elemental sulfur as a substrate does not require an initial addition of acid. The principal advantage of the microbiological processes is a considerable reduction in the usage of significant quantities of acid to solubilize metals.

When comparing the microbial processes with acid leaching treatment [11,12,25], some conclusions could be drawn:

- The indigenous adapted sulfur- or iron-oxidizing bacteria can be utilized for toxic metal removal from sludges.
- The use of a microbial leaching process with elemental sulfur and ferrous sulfate as substrates permits to considerably reduce the quantity of acid required for metal extraction with a reduction of 100% and 83%, respectively.
- Bioleaching process with sulfur as a substrate for sulfur-oxidizing bacteria was revealed to be better than the acid treatment process and microbial leaching with ferrous sulfate and iron-oxidizing bacteria for solubilization of all metals examined.
- Microbial leaching process with ferrous sulfate as a substrate permits a better solubilization of cadmium, copper, manganese, and zinc than the acid treatment with sulfuric acid. However, the solubilization of aluminum, chromium, nickel, and lead was less than that for acid leaching.

9.1.4.1 Alum Sludges

Q1 These sludges are usually fairly high in moisture content—98% or more. The BOD is low, about $50\,\mathrm{mg\,L^{-1}}$, but the COD is fairly high, from 500 to $1500\,\mathrm{mg\,L^{-1}}$. The pH of waste alum sludge is about 6, and ~40% of the solids are volatile. The major impact of these waste alum discharges is the formation of mudbanks along the stream.

One of the main problems of waste alum sludge is its very high moisture content. Thickeners have been used in some places to reduce this and make the sludge more efficient to handle. Tube settlers have been introduced for waste alum sludge and appear to be quite effective in increasing the solids concentration.

Dewatering waste alum sludge is difficult. The specific resistance of alum sludges is about $10\text{–}40 \times 10^{12}\,\mathrm{m\,kg^{-1}}$, which is approximately the same as activated sludge. Interestingly, the specific resistance of alum sludge decreases with increasing solids concentration. Alum sludges at even high solids concentrations behave as a liquid, with Newtonian flow characteristics. Centrifugal dewatering is possible with high polymer dosages. It has been found that a 2 lb polymer/ton of solids had almost no effect on solids recovery, but the addition of 1 lb polymer/ton more polymer resulted in a jump to better than 90% solids recovery. In other words, the recovery-polymer dose curves were very steep. Cake solids of about 15% were obtained, which was considered acceptable since a drying system followed centrifugation. Pressure filters are used to dewater alum sludges in a number of cities, with lime conditioning to aid the dewatering.

9.1.4.2 Lime Sludges

Lime CaO can be used for removing many of the impurities in wastewater. By adding sufficient quantities of lime, the pH can be raised to about 11.5 and calcium carbonate, metal hydroxides, and phosphates are precipitated. The phosphorus present is precipitated mostly as calcium hydroxyapatite $Ca_5(OH)(PO_4)_3$. The small quantities of aluminum, magnesium, and manganese oxides aid in the removal of silt and other impurities.

It is possible to recover lime from the sludge produced in lime precipitation. One method is to centrifuge the slurry at low solids recoveries so as to remove only the heavy $CaCO_3$. The magnesium

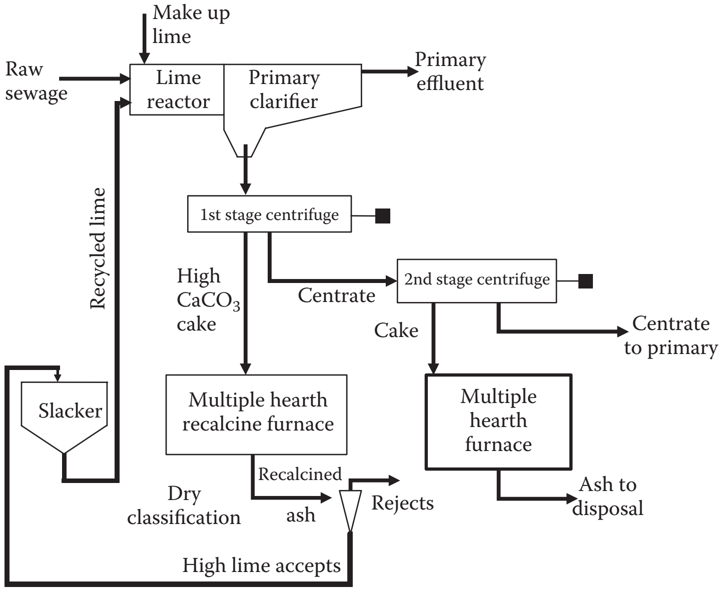

FIGURE 9.4 Sludge treatment by centrifugation.

hydroxide and other light solids are then dewatered in a second centrifuge (Figure 9.4). The $CaCO_3$ cake is then recalcined with the addition of heat according to the following reaction:

$$CaCO_3 \Leftrightarrow CaO + CO_2$$

The recalcination process is fairly simple because the cakes produced in centrifuges and vacuum filters are quite dry, with solids ranging from 40% to 50%. Lime sludges with a high pH, however, have proved difficult to dewater. The recalcination process can be conducted in a rotary kiln or in a fluidized bed furnace. In both cases, the CO_2 produced can be used to dissolve some of the hydroxides or for recarbonizing the finished water to bring the pH down. A recently completed study showed that the addition of lime to the primary clarifier produced a thick sludge that centrifuges and could easily process. Approximately 60% of the calcium carbonate fed to the first centrifuge was recovered in the cake, whereas 50–75% of the other solids were rejected as the centrate. The calcium carbonate slurry was subsequently dewatered to 50% solids and incinerated. The lime produced in recalcining is CaO or quicklime, a dangerous compound. It is often slaked by adding water following the reaction below and the resulting hydrated product $Ca(OH)_2$ is much safer to handle.

$$CaO + H_2O \Leftrightarrow Ca(OH)_2$$

Quicklime can also be used in the dewatering or drying of biological sludge by mixing the lime and sludge in a common concrete mixer. The above reaction is exothermic, and thus sludge is dried and disinfected as a result of the high temperatures produced. This process, used in some European treatment plants, yields a product that is marketable as a soil conditioner, especially where the soil is acidic; however, it lacks permeability and has poor water-holding capacity.

9.1.4.3 Iron Sludges

The sludges formed by both ferric and ferrous compounds are surprisingly soft and fluffy and difficult to dewater to more than 10% or 12% solids. Such sludges still behave as liquids. The recovery of iron from such operations is theoretically possible but not economically feasible.

9.2 ION EXCHANGE MATERIALS

Ion exchangers are insoluble granular substances that have in their molecular structure acidic or basic radicals that can exchange, without any apparent modification in their physical appearance and without deterioration or solubilization, the positive or negative ions fixed on these radicals for ions of the same sign in solution in the liquid upon contact with them [26]. This process, known as ion exchange, enables the ionic composition of the liquid being treated to be modified without changing the total number of ions in the liquid before the exchange.

For each reaction involving two ions A and B, the equilibrium between the respective concentrations A and B in the liquid and in the ion exchange substance can be shown graphically (Figure 9.5).

Under conditions of equilibrium, and for a concentration B of X% in the solution, the exchange material becomes saturated up to a concentration of Y%. When the two ions A and B have the same affinity for the exchange material, the equilibrium curve corresponds to the diagonal of the square. The more marked the exchange material's preference for ion B, the further the curve moves in the direction of the arrows. The form of the curve for a given system of two ions depends on a number of factors: nature and valence of the ions, concentration of ions in the liquid, and the type of exchange material. To achieve substantially complete exchange, it is necessary to create successive equilibrium stages by percolating the water through superimposed layers of exchange material (Figure 9.6).

If we take a layer of exchange material entirely in form A, and if a liquid containing ions B or B′ (the exchange material has a much greater affinity for ion B′ than for ion B) is passed through it, successive equilibrium points between (A and B) and (A and B′) give different series of concentration curves. The possible breakthrough or exhaustion curves (Figure 9.7) depend not only on the static equilibrium curve mentioned above, but also on the exchange kinetics between the liquid and the exchange material: this type of kinetics involves the penetration of solutes into the exchanger, and are governed by laws known as the "Donnan equilibrium laws."

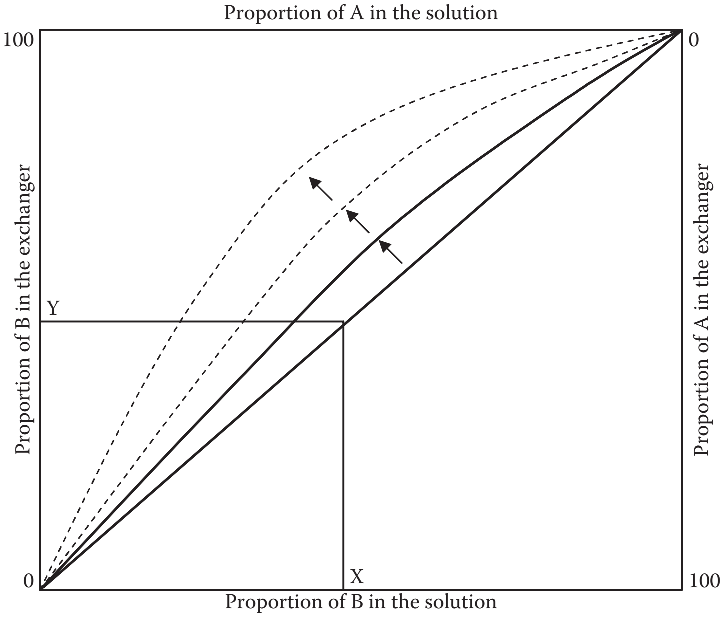

FIGURE 9.5 Ion exchange equilibrium curves.

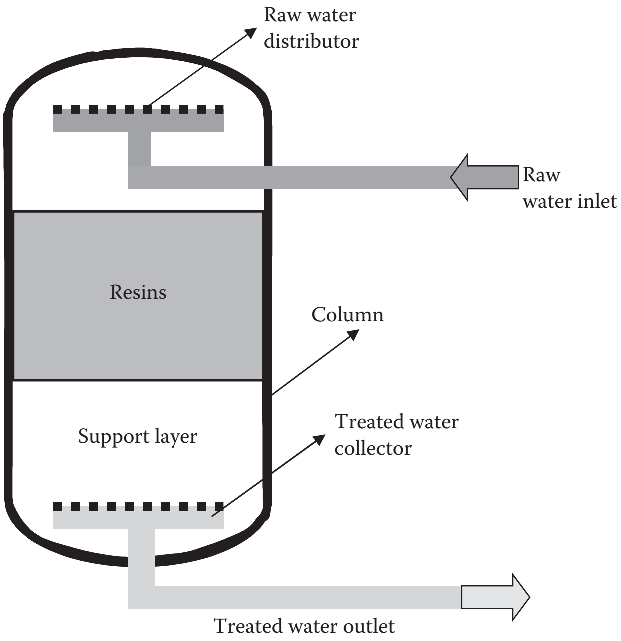

FIGURE 9.6 Common column filled with ion exchange material to treat raw polluted water.

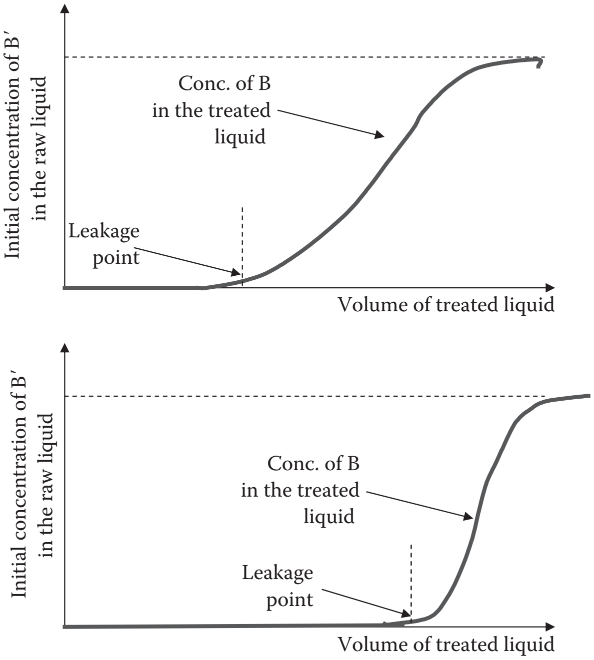

FIGURE 9.7 Exhaustion curves for an ion exchange material entirely in form A. The exchange material has a much greater affinity for ion B′ than for ion B.

The first ion exchange substances were natural earths (zeolites); they were followed by synthetic inorganic compounds (aluminosilicates) and organic compounds; the latter materials are used today almost exclusively and, derived from hydrocarbon feedstocks, they are called resins. This term has been often wrongly extended to cover just about any kind of ion exchanger.

Ion exchange resins have proven to be an efficient means of controlling the concentration of heavy metals in wastewaters. There is a noticeable and expanding activity in the application of ion exchange to the recovery and recycling of water and heavy metals from waste. There are various types of resins available for the removal of different metals from effluents. Each resin has certain advantages and limitations and a proper choice, depending on effluent composition, should be made for its application.

9.2.1 TYPES OF RESINS

Ion exchange resins are insoluble polymers with chemical active groups that, when ionized, bond with opposite-charged metal ions. Those resins capable of exchanging cations are called cation exchangers. Resins capable of exchanging anions are called anion exchangers. The ion exchange function of a resin is generally limited by pH levels, flow rate, turbidity, type of regenerant, and complexity of wastewater. Organic resins generally feature a complex matrix, a three-dimensional network of hydrocarbon chains [27]. According to the structure, there are two categories: the resins of the gel type and those of the macroporous or loosely cross-linked type. Their basic macromolecular structure is identical, obtained in both cases by copolymerization of, for example, styrene and divinylbenzene. The difference between them lies in their porosity. Their high cross-linking degree increases their mechanical strength to both physical (pressure—negative pressure) and chemical (change in the ionic saturation, or exhaustion state) stresses. Gel-type resins have a natural porosity that results from the polymerization process and is limited to intermolecular distances. It is a microporous-type structure. Macroporous-type resins have an additional artificial porosity that is obtained by adding a substance designed for this purpose. Thus, a network of large canals known as macropores is created in the matrix. These products have a better capacity for adsorption and desorption of organic substances.

The cation exchangers can be categorized into two groups: strong acid and weak acid. Anion exchangers can also be divided into strong base and weak base groups. Those resins that remove a specific metal ion are known as chelating exchangers. Tables 9.4 and 9.5 summarize the physical and chemical characteristics of the macroporous- and gel-type resins as well as the main suppliers of these types of ion exchangers.

9.2.1.1 Strong Acid Cations

They are characterized by having HSO_3 sulfonic radicals and acidities close to that of sulfuric acid. In current use these are sulfonated polystyrenes obtained by

- Copolymerization of styrene and divinylbenzene in emulsion form to obtain perfect spheres on solidification
- Sulfonation of the beads thus obtained.

The products obtained by this process are virtually monofunctional. Their physical and chemical properties vary depending on the percentage of divinylbenzene to styrene which, in turn, determines the degree of cross-linking, generally varying from 6% to 16%.

The ion exchange process follows the general reaction of this type:

$$RSO_3^-H^+ \Leftrightarrow RSO_3^-Na^+ + H^+$$

TABLE 9.4
Physical and Chemical Characteristics of Gel Resins (Strong Acid, Weak Acid, Strong Base, and Weak Base) as Well as the Main Suppliers of These Types of Ion Exchangers

Resins/Gel	Strong Acid	Weak Acid	Strong Base	Weak Base
Particle diameter (mm)	0.3–1.2	0.3–1.2	0.3–1.2	0.3–1.2
Moisture content (%)	45–48	46–53	45–48	46–53
pH range	0–14	1–14	0–14	1–14
T maximum (°C)	120	120	120	120
Turbidity tolerance (NTU)	5	5	5	5
Tolerance ($g\,m^{-3}$)	Chlorine 1.0	Iron 0.5	Chlorine 1.0	Iron 0.5
Total capacity ($eq\,L^{-1}$)	1.4–2.2	3.5–4.2	1.2–1.4 (type I) 1.3–1.5 (type II)	1.4–2.0
Regeneration	NaCl 80–300 H_2SO_4 80–250 HCl 40–200	110% of the capacity used	NaOH 40–100 NH_3 30–60 Na_2CO_3 60–130 NaOH 40–200	—
Supplier				
Bayer	Lewatit S100		Lewatit M 500 (I) 600 (II)	
Duolite	Duloite C20	Duloite C433	Duloite A101 (I) 102 (II)	
Dow Chemical	Dowex HCR-S	Dowex CCR-2	Dowex SBR (I) SAR (II)	Dowex WGR-2
Rohm&Haas	Amberlite IR120	Amberlite (IRC50, IRC84)	Amberlite IRA 400 (I) 410 (II)	Amberlite IRA68

Notes: The total exchange capacities of various categories of exchange materials are expressed in gram equivalents per liter of resin. The values of regeneration levels listed above are expressed in grams of pure product per liter of resin.

The selectivity of these resins is usually as follows:

$$Fe^{3+} > Al^{3+} > Ca^{2+}$$
$$La^{3+} > Y^{3+} > Ba^{2+}$$
$$Th^{4+} > Hf^{4+} > Zn^{2+}$$
$$Ac^{3+} > La^{3+}$$
$$Th^{4+} > La^{3+} > Ce^{2+} > Na^{+}$$
$$Mg^{2+} > Be^{2+}$$

9.2.1.2 Weak Acid Cations

These are polyacrylic resins characterized by the presence of HCO_2 carboxyl radicals that can be likened to organic acids such as formic or acetic acid. They differ from strong acid exchangers in two respects:

- They retain only the Ca, Mg, Na, and so on, cations that are bound to bicarbonates, but they cannot exchange cations at equilibrium with strong anions (SO_4, Cl, and NO_3).
- They can be regenerated more easily and their regeneration rates are close to those of stoichiometric efficiency.

The ion exchange process follows the general reactions of this type:

$$RCO_2H \Leftrightarrow RCO_2^- + H^+$$

$$RCO_2H + HCO_3^- + Na^+ \Leftrightarrow RCO_2^-Na^+ + H_2O + CO_2.$$

TABLE 9.5
Physical and Chemical Characteristics of Macrosporous Resins (Strong Acid, Weak Acid, Strong Base, and Weak Base) as Well as the Main Suppliers of These Types of Ion Exchangers

Resins/Macroporous	Strong Acid	Weak Acid	Strong Base	Weak Base
Particle diameter (mm)	0.3–1.2	0.3–1.2	0.3–1.2	0.3–1.2
Moisture content (%)	40–46	52–57	40–46	52–57
pH range	0–14	5–14	0–14	5–14
T maximum (°C)	150	150	150	150
Turbidity tolerance ($g\,m^{-3}$)	5	5	5	5
Tolerance ($g\,m^{-3}$)	Chlorine 1.0	Iron 0.5	Chlorine 1.0	Iron 0.5
Total capacity ($eq\,L^{-1}$)	1.7–1.9	2.7–4.8	1.0–1.1 (type I) 1.1–1.2 (type II)	1.2–1.5
Regeneration	NaCl 80–300 H_2SO_4 80–250 HCl 40–200	110% of the capacity used	NaOH 40–100 NH_3 30–60 Na_2CO_3 60–130/ NaOH 40–200	—
Supplier				
Bayer	Lewatit SP112	Lewatit CNP80	Lewatit M 500 (I) MP 600 (II)	Lewatit MP64
Duolite	Duloite C26	Duloite C464	Duloite A 161 (I) 162 (II)	Duloite A378
Dow Chemical	Dowex MSC-1		Dowex MSA1 (I) MSA2 (II)	Dowex MWA-1
Rohm&Haas	Amberlite IR200		Amberlite IRA 900 (I) 910 (II)	Amberlite IRA93

Notes: The total exchange capacities of various categories of exchange materials are expressed in gram equivalents per liter of resin. The values of regeneration levels listed above are expressed in grams of pure product per liter of resin.

The selectivity of these resins is usually as follows:

$$H^+ > Ca^{2+} > Mg^{2+} > K^+ > Na^+.$$

9.2.1.3 Strong and Weak Base Anions

Anion exchangers can be divided into weak or intermediate and strong base anion exchangers. These two types can be distinguished in practice as follows:

- The weak base types do not retain very weak acids such as carbonic acid or silica, but the strong base types retain them completely.
- The strong base types alone are able to release the bases from their salts following the typical reaction:

$$R\text{–}OH + NaCl \Leftrightarrow R\text{–}C + NaOH.$$

- The weak base types are more or less sensitive to hydrolysis, in the form of the displacement, by pure water, of the anions previously attached to the resin:

$$R\text{–}Cl + H_2O \Leftrightarrow R\text{–}OH + HCl.$$

  The strong base types are practically unaffected by this phenomenon.
- The weak base types are regenerated more easily.

The existence of quaternary ammoniums in the molecule is typical of the strong base anion exchangers. All the strong base resins used for demineralization purposes belong to two main groups commonly known as type I and type II. The former consists of simple quaternary ammonium radicals, and the latter consists of quaternary ammonium radicals with alcohol function. Each type has its own field of application, depending on the nature of the water to be treated and the conditions applying to the regeneration cycle. The two types differ in the following respects:

- In type I, the basicity is strong and the capacity low; the regeneration efficiency is poor.
- In type II, the basicity is weaker and the capacity higher; the regeneration efficiency is also better.

The weak anion exchangers consist of a mixture of primary, secondary, tertiary, and sometimes quaternary, amines. The nucleus of the molecule is highly varied in nature and may be aliphatic, aromatic, or heterocyclic.

The exchange process of the strong base type follows the reaction:

$$R_4N^+OH^- + H^+ + A^- \Leftrightarrow R_4N^+A^- + H_2O.$$

The selectivity is as follows:

$$NO_3^- > CrO_4^{2-} > Br^- > SCN^- > Cl^-.$$

The exchange process of the weak base type follows the reaction:

$$R_3N + H^+ + A^- \Leftrightarrow R_3NH^+A^-.$$

The selectivity is as follows:

$$OH^- > SO_4^{2-} > CrO_4^{2-} > NO_3^- > PO_4^{3-} > MoO_4^{2-} > HCO_3^- > Br^-.$$

9.2.1.4 Adsorbent Resins

These are products that are designed to retain nonionic compounds (basically organic molecules) in solution in polar and nonpolar solvents by means other than ion exchange and by a reversible technique. This process of adsorption on solids is very complex and involves various types of interaction between the adsorbent surface and the adsorbed molecules. For this reason, the adsorptive capacity of the resins depends on numerous factors such as the chemical composition of the skeleton (polystyrenic, polyacrylic, and formophenolic), the type of functional groups of polar adsorbents (secondary and tertiary amines, quaternary ammonium), the degree of polarity, the porosity (usually macroporous materials with pore sizes up to 130 nm), the specific surface area: up to 750 $m^2\,g^{-1}$, the hydrophilic nature, and the shape of the grains.

Their possible uses include the following:

- Protection of the ion exchange system by retaining the pollutants present in feed water (humic acids, detergents, etc.)
- Decolorization of sugar syrups, glycerin, grape musts, whey, and so on
- Separation, purification, and concentration processes in the pharmaceutical industry and synthetic chemistry.

The regeneration method of adsorbent resins basically depends on the product adsorbed. The traditional eluants are acids, bases, sodium chloride, methanol, adapted organic solvents, and, in certain cases, pure water or steam.

The choice of the correct adsorbent presents some difficulty; it must be guided by the properties of each adsorbent and the products to be retained. Therefore, laboratory or pilot studies are indispensable in the majority of cases.

9.2.1.5 Special Resins

Polyfunctional resins: these are products that combine the properties of strong resins with those of weak resins. This is the case with anion resins that are able to remove all the anions including silica and CO_2 while ensuring a high exchange capacity and an excellent regeneration efficiency due to their weak-base function.

Chelate resins: These comprise special functional groups (aminophosphoric, aminodiacetic, aminodioxime, mercaptan) that permit the selective retention of heavy metals from various effluents (zinc, lead, mercury, etc.), gas chromatographic separations of metals, and also the final softening of brine from the electrolysis process.

Resins for nuclear use: These involve products with a higher degree of purity than that of resins used in common operations. Among these are strong acid cation resins in H^+ form that are regenerated to 99%, and strong base anion resins in OH form with less than 0.1% of Cl^-.

Catalyzing resins: These conventional resins are used in a basic or acidic catalyst process (e.g., the inversion of glucose in the manufacture of liquid sugar). They could also be used with a metallic catalyst (e.g., a palladium resin for deoxygenation of demineralized water or sea water).

9.2.2 SPECIFIC APPLICATIONS

It is important to emphasize that the techniques related to ion exchange processes should not be used unless the raw water has been subjected to a form of preliminary treatment suited to its type, which must include the removal of suspended solids, organic matter, residual chlorine, chloramines, and so on. The continuous removal of heavy metals by ion exchange takes place in fixed-bed columns that are packed with cationic and/or anionic resins. The metals sorb onto the resins in exchange of hydroxide anions, protons, and/or light metal cations that are released into the solution. An ion exchange system can perform both heavy metal removal and neutralization of acidic water. Furthermore, ion exchange systems open the possibility of recovering heavy metals in the form of liquid concentrates. These concentrates can be either returned to the manufacturing process, or they can be

- Efficiently precipitated yielding small volumes of sludges for disposal or metal recovery
- Further processed directly to recover the metal(s) in solid and resaleble (reusable) form.

The higher the selectivity of a resin, the more strongly the metals are bound to it, and the more difficult it usually is to desorb them. This increases the consumption of a regenerant and hence the operating cost. Moreover, the resins are prone to fouling (poisoning) by organic substances [28]. Finally, as ion exchange resins are hydrocarbon based, their price is coupled with the price of crude oil and they are thus relatively expensive, with the price per kilogram ranging from USD10 to USD50 (prior to the year 2004). Therefore, in order to keep the operating cost sufficiently low, the ion exchange processes are usually applied only to effluents containing medium or low levels of heavy metals.

9.2.2.1 Nickel

The most commonly applied process for removal of nickel from wastewater is in the use of a strong acid cation resin. Unfortunately, this type of resin can only be applied if nickel is the only polyvalent metal ion in the wastewater. Consider a wastewater composed of nickel in the presence of ammonium molybdate. The nickel is most effectively recovered by the use of an aminophosforic acid resin. The Russian-made chelating resin ANKF-80 used on a wastewater at pH 2 is approximately 19 times more effective than a conventional resin. Also available, but not as effective, is the Amberlite

XE-318, having an ion capacity of 34 g L^{-1} of resin. Another type of resin effective in nickel removal is a weak acid resin. This type of resin shows high selectivity for nickel ions even in wastewater polluted with organic carbon. A Wofatit CA-20 resin is the most effective weak acid resin manufactured and available. Another weak acid resin available is the Zerolit 236 possessing an ion capacity of 108 g L^{-1} of resin. The regenerant used for these resins is ammonium carbonate.

Strong acid resins such as Zerolit 525, Amberlite IR-20, and Amberlite 200 have ion capacities of 48, 31, and 30 g L^{-1} of resin, respectively. The regenerant used is again ammonium carbonate.

9.2.2.2 Copper

In the industrial production of copper, large amounts of acidic wastewaters are produced. There are mainly two specific types of resins applied for copper recovery. One resin is Dowex XFS-4195. This *N*-(hydroxyalkyl) picolyamines-based resin can be applied for very acidic wastewaters. Another resin, having the same base, is Dowex XFS-4196, which performs well for wastewaters of higher pH. The regenerant used in both cases is sulfuric acid.

Unfortunately, not all wastewaters can be purified of copper with ordinary ion exchangers. Wastewaters that contain organic ligand, for example, cannot be treated in this way because they form a coordination complex. Complex compounds having carboxylic acid groups such as tartaric, citric, and lactic acids will interfere with the efficiency of a standard ion exchanger. In these cases the stability for the copper complexes are lower. The chelating resin will successfully remove copper ions from such wastewaters.

9.2.2.3 Zinc

Zinc can be extracted from wastewaters as a Zn^{2+} cation or $ZnC1_4^-$ anion. The zinc cation may be sorbed by a cation exchanger or a chelating resin and the anion by an anion exchanger. Zinc salts are present in wastewaters from, for example, the kaolin industry and the blowdown of cooling towers. For the kaolin industry, a strong acid resin may be employed for the removal of the Zn^{2+} cation, using sodium chloride as a regenerant. In the case of the cooling tower blowdown water, phosphoric acid resins such as Duolite ES-63 or Duolite TSAP-40 are commonly employed.

9.2.2.4 Mercury

As a metal, mercury is probably one of the worst water pollutants. The source of most mercury pollution is the wastewater produced from chlorine and alkali manufactures. Resins containing the thio group possess high affinity for mercury ions. The Imac-TMR resin is an example. Their operational capacity depends on the concentration of mercury present in the wastewater (see Table 9.6).

Other types of molecules that exhibit high affinity for mercury ions contain the R–S–C(NH)–NH_2 (isothiouronium) group, an example of which could be resin Srafion-NMRR. Another highly active chemical group is R–NH–C(S)–SH, the dithiocarbonate group, which is found in the resin Nisso-ALM-125. Regeneration using sulfuric acid is applied to recover mercury from the resin.

TABLE 9.6
Operational Capacity of a Resin to Uptake Mercury

Hg Concentration (mg L^{-1})	Capacity for Hg (g L^{-1} of Resin)
0.6	48
0.8	57
1.0	66
4.0	80
6.0	88
8.0	95
10.0	100

Another resin available is the Nisso-ALM-126 whose capacity can be increased by heating the resin to a maximum of 50°C. Regeneration is not feasible in this case. However, the mercury can be removed from the resin by roasting it. Strong base resins can also be applied for the removal of mercury from wastewaters. For acidic wastewaters within a pH range of 2.5–3.5, Wofatit SDW or Varion AD resins can be used. They possess the ability to remove up to 85% of the mercury. The use of a strong acid resin such as the Amberlite IR-120 could produce an effluent containing levels of 0.05 mg L^{-1} of Hg^{2+} from the initial solution containing 10 mg of Hg^{2+} per liter of wastewater.

9.2.2.5 A Case Study

A typical and ubiquitous industrial operation known to have a metal-pollution problem is metal plating. The amount of electroplating process effluent encountered in an average size operation generally varies between 25,000 US gal day^{-1} and 100,000 US gal day^{-1}. For the case design calculations, the wastewater flow of 48,000 US gal day^{-1} (182.4 $m^3 day^{-1}$) has been chosen. It is assumed to contain 20 mg $Zn^{2+} L^{-1}$, 30 mg $Ni^{2+} L^{-1}$, 40 mg $CuSO_4 L^{-1}$, and 130 mg $CrO_3 L^{-1}$. The latter chromium content eventually complicates the treatment system considerably as will be demonstrated in the design of the treatment facility. Removal of the basic metals from the given solution is considered as a major objective. Chromium is a valuable element and its recovery would be highly desirable. However, since it cannot be in its chromate form retained on the same cationic ion exchanger as all the other metals, a special sequence of additional two ion exchange operations would have to be added to the basic cationic one. A typical treatment system is outlined in Figure 9.8. The pH of the solution to be treated has a crucial effect on the uptake of metals from acidic solutions. The resin IRC-718 selected for the treatment process is more selective for metal ions and calcium interference is minimized at the optimum operation pH 4. Requirement for this pH level dictates the necessity of a pH adjustment in a tank that has to be placed prior to the sorption contact stage. Following the pH adjustment, the wastewater solution should be filtered to remove precipitates, particulate matter, and insoluble salts from the solution. The filtration step decreases the possibility of resin fouling.

The solution to be treated is pumped into two columns operating in a sequence. The whole arrangement could operate for five days until saturation of the bed. For practical reasons, it may be more convenient to regenerate the first column approximately half-way through this period, whereas the second one becomes first in their sequence. The newly regenerated column would be always

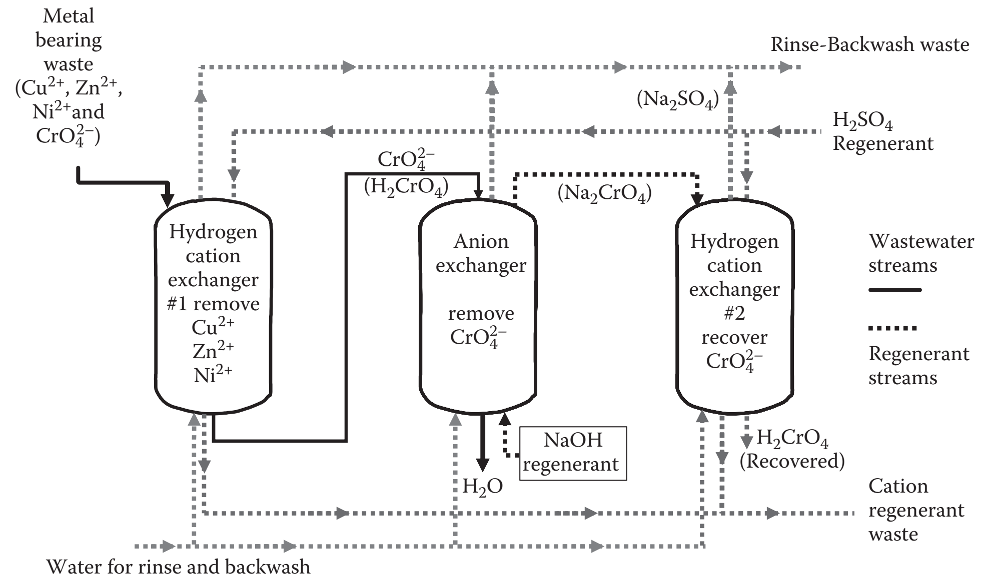

FIGURE 9.8 Ion exchange process: Schematic diagram of a case study.

phased in as a polishing second one in that sequence. This arrangement would require three columns, two operating whereas the third one would be on the regeneration cycle. The columns are designed to be backwashed to move any entrained solids under up-flow conditions. The partly fluidized bed expansion of 50% has been estimated for this operation. Regeneration is done with 5% of sulfuric acid. The operations of backwashing, regeneration, and rinsing are done *in situ*, in the same columns. The spent regenerant and rinse water from this first cationic exchange contain metal sulfates, $M_2(SO_4)_n$, and some sulfuric acid. They must therefore be neutralized in a separate operation and the metals precipitated prior to discharge to any receiving body.

9.3 REVERSE OSMOSIS

Reverse osmosis is based on the separation of the solvent from the influent waste stream by a pressure in excess of the osmotic pressure of the solution. The wastewater flows under high pressure through an inner tube made of a semipermeable membrane material. The purified solvent is removed from the outer tube, which is at atmospheric pressure (Figure 9.9) [29].

The disadvantages associated with reverse osmosis involve the sensitivity of the membrane. Organics as well as other impurities precipitate, which leads to membrane fouling. It is therefore necessary to have a consistent composition of the influent waste stream. Apart from the membrane sensitivity, the process also requires elevated pressures that drive up the operating costs of pumping.

9.3.1 PRINCIPLE OF REVERSE OSMOSIS

Reverse osmosis makes use of the properties of semipermeable membranes that allow water to pass through while solutes are retained except for certain organic molecules very similar to water (with a low molecular weight and strong polarity). If a concentrated saline solution is separated from a more dilute solution by such a membrane, the difference in chemical potential tends to promote the passage of water from a compartment with a low potential to that with a higher potential in order to dilute it (natural osmosis). To stop this diffusion, a pressure must be exerted on the "filtered" fluid. At equilibrium, the pressure difference established in this way is known as the osmotic pressure of the system (Figure 9.10).

A simple equation (9.1) relates osmotic pressure to concentration:

$$\Pi = \Delta C * R * T, \tag{9.1}$$

where Π is the osmotic pressure (Pa), ΔC is the difference in concentration in $\mathrm{mol\,m^{-3}}$, R is the constant of an ideal gas = 8.314 ($\mathrm{J\,mo1^{-1}\,K^{-1}}$), and T is the temperature in degrees kelvin.

Clearly, the smaller the molecule (i.e., the lower the molecular weight), the greater the osmotic pressure set up by the same difference in concentration. This explains why ultrafiltration leads to an osmotic backpressure that is much lower than that experienced with reverse osmosis.

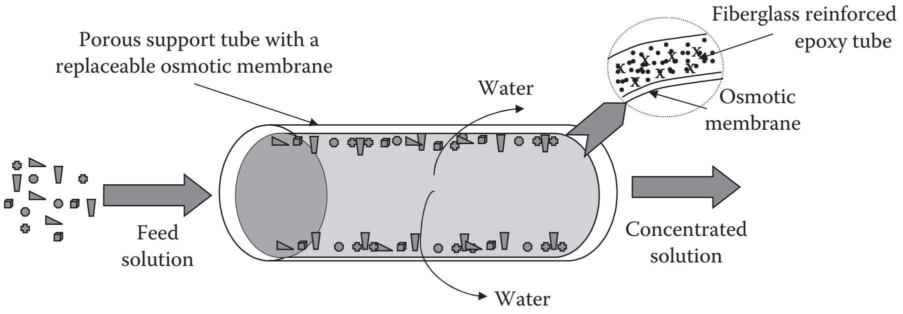

FIGURE 9.9 Tubular module section of a reverse osmosis operation.

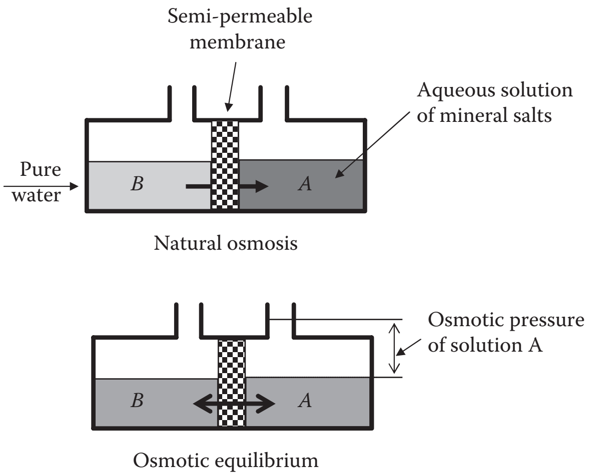

FIGURE 9.10 Osmosis phenomenon.

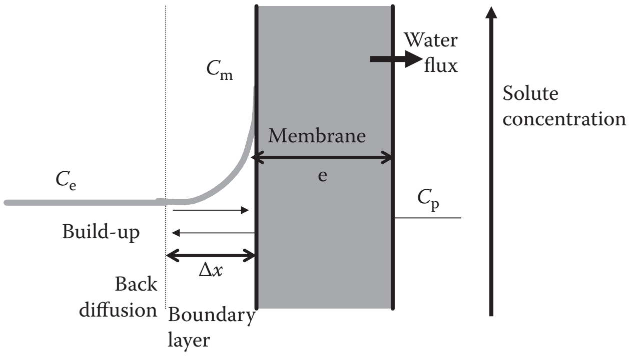

FIGURE 9.11 Concentration polarization during a reverse osmosis process.

In fact, to produce "pure" water from a saline solution, the osmotic pressure of the solution must be exceeded. In the same way, in order to obtain economically viable flows, at least twice the osmotic pressure must be exerted. For instance, for a brine containing several grams of salt per liter, pressures of 5–30 bar would be needed, and for sea water, pressures of 50–80 bar would be needed. A second phenomenon can amplify this effect.

As Figure 9.11 illustrates, when water is transferred, the molecules and ions retained by the membrane tend to accumulate along its entire surface, thereby increasing both the salinity actually "treated" by the membrane and the osmotic pressure that must be "overcome" in order to desalinate the solution. This results in higher energy costs, as well as in the risk of causing precipitation if the solubility product of one of the cation–anion couples is exceeded in the boundary layer all along the membrane.

This phenomenon is known as concentration polarization of the membrane and it is defined by the coefficient Ψ (Equation 9.2):

$$\Psi = \frac{C_m}{C_e}, \tag{9.2}$$

where C_m is the concentration of the liquid in contact with the membrane and C_e is the concentration of the liquid to be treated.

The concentration polarization phenomenon can be reduced to a minimum by maintaining a circulation flow across the upstream surface of the membrane. That limits the thickness of the boundary layer and facilitates the reverse diffusion of the rejected solutes; however, this also limits the fraction of desalinated water. This technique is used in industrial systems to maintain the coefficient Ψ between 1 and 1.4.

To describe the phenomena observed, best models call upon the laws of diffusion, water being considered dissolved by the polymer making up the membrane (water used for swelling the polymer); this water moves under the effect of the pressure gradient, whereas the salts move under the effect of their concentration gradient alone.

For a saline solution, the water and salt flux rates may be obtained by Fick's and Henry's laws for water (Equation 9.3) and for salts (Equation 9.4):

$$Q_p = K_p \frac{S}{e} (\Delta P - \Delta p) K_t, \tag{9.3}$$

where Q_p is the flow of water through the membranes, K_p is the membrane permeability coefficient for water, S is the membrane surface area, e is the thickness of the membrane, ΔP is the hydraulic pressure differential across the membrane, Δp is the osmotic pressure differential across the membrane, and K_t is the temperature coefficient.

Thus, the flow of water through the membrane is directly proportional to the effective pressure gradient, represented by the difference between the hydraulic and the osmotic pressure.

The coefficient K_t takes the viscosity of water into account. The latter decreases when the temperature rises. Therefore, the flow *is* greater when the temperature rises (2.5–3% difference per degree at about 15°C).

$$Q_p = K_s \frac{S}{e} (\Delta C) K_t, \tag{9.4}$$

where Q_s is the flow of salt through the membrane, K_s is the membrane permeability coefficient for solutes, S is the membrane surface area, e is the thickness of the membrane, ΔC is the ion concentration differential across the membrane ($C_m - C_p$ or $C_e * \Psi - C_p$), and K_t is the temperature coefficient.

The flow of salt is directly proportional to the gradient of concentration through the membrane; for a given membrane and a given solution, its value is independent of the applied pressure.

In practice, Table 9.7 summarizes the general tendencies in all reverse osmosis systems.

9.4 ELECTROCHEMICAL PROCESSES, ELECTROWINNING

Public concern over water contamination and the steep rise in heavy metal prices triggered both governmental and industrial activity in the removal and recuperation of heavy metals from domestic and particularly from industrial wastewater. As the world consumption of resources increases,

TABLE 9.7
General Tendencies in Reverse Osmosis Systems

	Product Flow Q_p	**Product Salinity C_p**
Pressure ↑	↑	↓
Temperature ↑	↑	=
Salinity ↑	↓	↑
Ψ ↑	↓	↑

reserves will exhaust themselves even faster and the need for recycling is becoming more and more urgent. Traditionally, heavy metals are removed using precipitation (Section 9.1) or ion exchange methods (Section 9.2). Particularly, the most widely practiced precipitation, however, produces highly toxic sludge for which disposal is difficult and expensive. Electrolytic techniques can recuperate these metals from wastewater solutions either directly or when preconcentrated by ion exchange. Metals can then be profitably salvaged for resale and reuse. Six major electrochemical metal recovery methods will be discussed in detail: electrodialysis, forced flow, rotating cathode, mesh, packed bed, and fluidized bed recovery cells [25]. Generally, the capital costs for electrochemical processes range between two and three times the capital cost for a physico-chemical removal system. The operating costs are lower than physico-chemical systems due to the salvage value of the metal and the absence of chemical reagents [30,31].

9.4.1 BACKGROUND

In electrochemical processes, an electric potential is used to move charged ionic particles in solution from one medium to another [32] (Figure 9.12). For example, positively charged metal ions can be plated out on an electronegative cathode by applying a potential in an electrolyte solution. By varying the electric potential, metals can be plated out selectively. Problems in removing metals even in concentrations below 200 mg L^{-1} using electrolytic methods have been overcome, thus providing industries with the tools to reduce concentrations below government guidelines. The problems of dilute electroplating are due to the low mass transfer rate of migrating ions in solution. As Fick's law states, the mass transfer rate decreases with decreasing concentration gradient, resulting in lower rate at which metal plates on the cathode. As the plating-out rate decreases, so does the efficiency of the process. Furthermore, creation of hydrogen gas at the cathode surface due to the redox reaction creates an additional barrier for metal ions to plate on the cathode. These two problems can be solved by either having very large cathode surfaces (flow-through processes) or by increasing turbulence in the solution (flow-by processes). Mesh, packed bed, and fluidized bed cathodes are examples of flow-through cathodes, whereas forced flow and rotating cathodes are examples of flow-by processes [31,33]. Figure 9.13 represents a general metal (nickel) recovery treatment using an electrochemical cell process in conjunction with cation- and metal-selective exchangers.

9.4.2 FORCED FLOW CELL (FLOW-BY CATHODE)

A forced flow cell is characterized by a mechanical or physical agitation of the contaminated solution around the cathode. The agitation can be created either by intensive solution circulation by

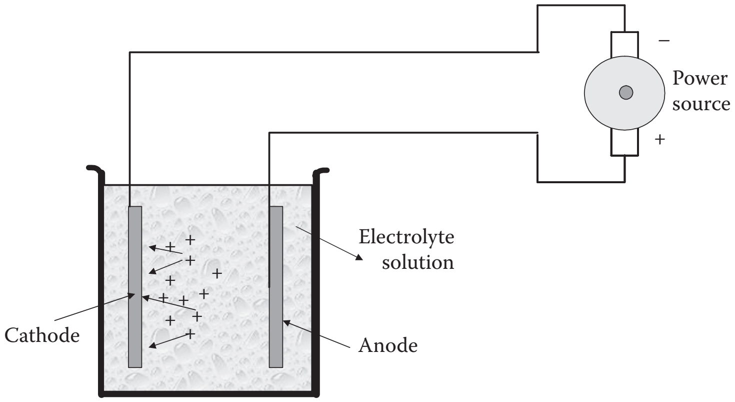

FIGURE 9.12 Electrochemical cell. Direction of travel of cations in an electrolyte solution applying a potential.

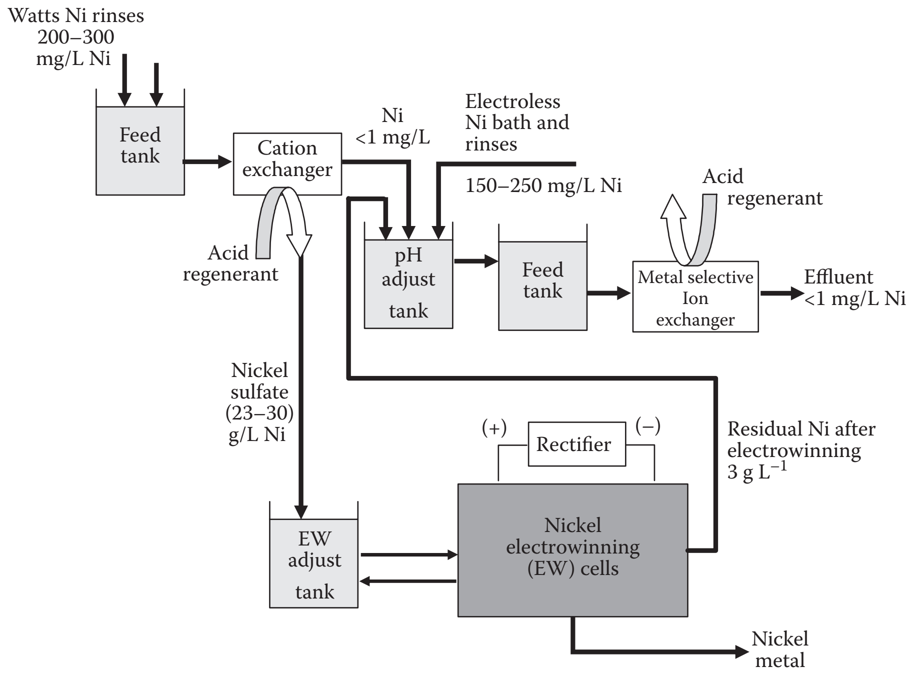

FIGURE 9.13 Nickel recovery treatment using an electrochemical cell process in conjunction with cation- and metal-selective exchangers.

using pumps or by venturies that introduce air bubbles at the bottom of the cell or by using static mixers. Since the process mechanism is simple, operating and capital costs are low. The metal is also easily recoverable since it plates out directly on flat immobile cathodes. However, the process suffers from low efficiencies when heavy metal concentrations are below 50 mg L^{-1} and cannot be made continuous due to the periodic removal of the cathodes for stripping. Owing to its low operating cost and good efficiencies above 50 mg L^{-1}, forced flow cells are often used in conjunction with preconcentration ion exchange or physico-chemical processes that are inexpensive and very efficient at concentrations below 50 mg L^{-1}. Figure 9.14 represents a general process scheme combining electrochemical, physico-chemical, and ion exchange treatments.

9.4.3 ROTATING CATHODES (FLOW-BY CATHODE)

As in forced-flow cells, the solution is agitated in order to increase the efficiency of the process. The difference resides in the fact that the agitation of the solution is accomplished by the brisk movement of the cathode. The most common arrangement is the rotation and impaction of cylindrical cathodes. Due to the process simplicity, the operating and capital costs are low. Furthermore, the process can be made continuous by impacting the rods together or by scraping the rods while in movement, and by collecting the metals as powder at the bottom of the cell. The process, however, still suffers from low efficiencies when concentration decreases below 50 mg L^{-1} and from possible breakdown problems due to the many moving parts. Figure 9.15 represents an electrowinning system using a rotating electrode to improve metal yields and allow economic metal recovery from solutions with lower metal concentrations.

9.4.4 MESH CATHODE (FLOW-THROUGH CATHODE)

Although flow-by cathodes are essentially two-dimensional cathodes, since their thickness is irrelevant, mesh cathodes and other flow-through cathodes are three dimensional due to the particulate

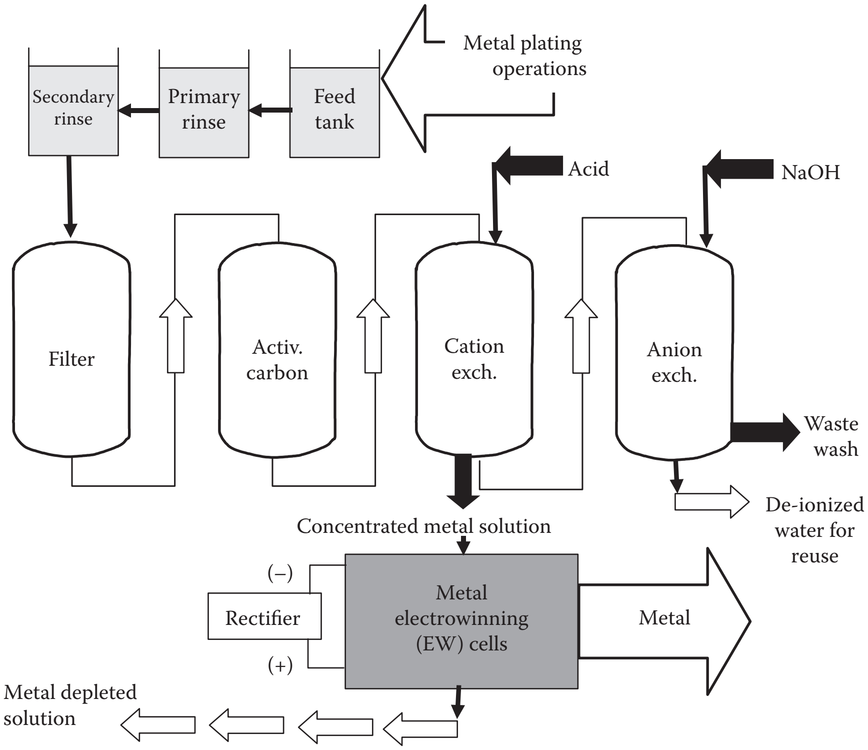

FIGURE 9.14 Ion exchange/physico-chemical/electrochemical combination.

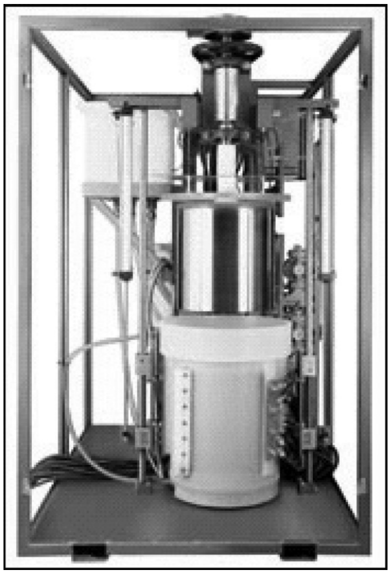

FIGURE 9.15 An electrowinning system using a rotating electrode to improve metal yields and allow economic metals recovery from solutions with lower metals concentrations.

or fibrous nature of the cathode. Flow-through cathodes can also be distinguished by their very high real-to-apparent surface area ratio that can reach 10,000. The mesh cathode consists of an intertwining matrix of conducting fibers through which the contaminated solution flows and on which the metal deposits. The heavy metal can be recovered by using the mesh cathode as the anode in

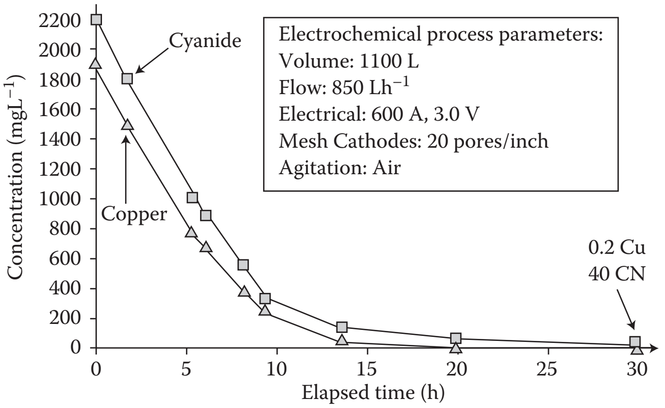

FIGURE 9.16 Kinetics of copper and cyanide electrochemical removal using a mesh electrode. The process parameters are indicated as a legend.

a conventional plating cell and by stripping the metal from the flat cathode. Mesh cathodes cells have low removal limits (0.5 mg L^{-1}) and low capital costs due to the simplicity of the plating mechanism. As an example, Figure 9.16 represents the kinetics of copper and cyanide electrochemical removal (using a mesh electrode) from a heavy-metal-laden wastewater. It appears that after 30 h, the removal of 98% and 99% could be reached for cyanide and copper, respectively. However, some problems do exist in the operation of mesh cathodes: blockage in the mesh due to large particles being caught in the matrix or by unequal depositing of metals in the mesh, batch processing of the solution, and high operating costs due to the complicated process of recovering the heavy metals.

9.4.5 Packed Bed Cells (Flow-through Cathode)

As in mesh cathodes, packed bed cells excel due to the high surface area of the cathode [34]. However, packed bed cathodes are made of packed metallic particles and not fibers such as in mesh electrodes. The particles are made of the same metal as the one being recuperated. The heavy metals plate out on the particle surface and are recuperated by either scraping off the metal from their surface or by melting them. Packed bed cells have the advantages in giving low residual metal concentrations (0.1 mg L^{-1}) and in the easy recuperation of heavy metals from the cathode. However, some inherent problems have made this process inaccessible to large industrial applications: high capital and operating costs due to the complicated mechanism, channeling in the bed, difficulties in scaling up of the process, high power consumption, and the batch processing of the solution.

9.4.6 Fluidized Bed Cells (Flow-through Cathode)

Fluidized bed cells are being examined very closely due to their low removal limit (0.1 mg L^{-1}) [35]. Furthermore, some problems associated with packed bed cells are eliminated in fluidized flow. Fluidized bed cells differ from packed bed cells due to the circulating motion given to the particles by fluidizing the particle bed with the contaminated solution. Apart from low metal removal limits, fluidized bed cells also take advantage of easy metal recovery from the particulate cathode and, unlike packed bed cells, the possibility of making the process continuous by bleeding the particles in a recycle stream. Once again, the complexity of the process makes fluidized bed cells rather expensive. Problems with channeling and scale up and the high power consumption have also left the process at the experimental stage.

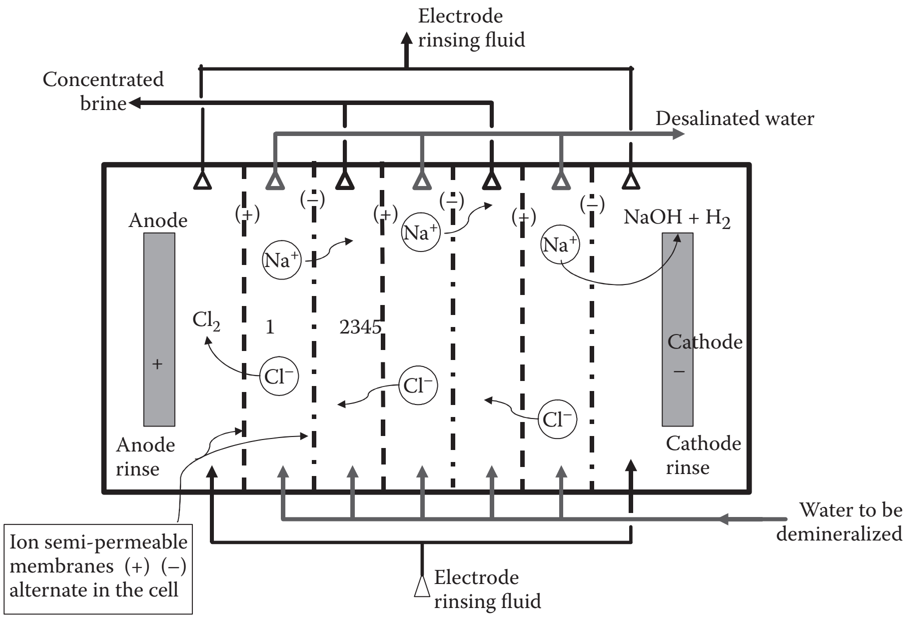

FIGURE 9.17 The principle of electrodialysis.

9.4.7 ELECTRODIALYSIS

Although electrodialysis does not remove heavy metals from solution, this process has proved very effective in concentrating heavy metals in the "brine" solution while simultaneously purifying the contaminated stream [36]. This is accomplished by separating a contaminated solution with an ion selective membrane and by applying an electrical potential across the system. As the potential is applied, cations (e.g., heavy metals in solution) migrate through semipermeable membranes toward the cathode, thus becoming concentrated in one solution compartment while the in-flow solution becomes purified. The concentrated solution can then be returned to an electroplating cell. Figure 9.17 represents the principle of the electrodialysis process. In the past, electrodialysis was limited by the strength, high cost, and efficiency of the cation selective membrane. However, continued improvements in membrane properties have resulted in day-to-day improvements of the electrodialysis process. The most attractive aspect of the process is the selective extraction performance of the membrane. For the present, its high removal limits ($30\,\mathrm{mg\,L^{-1}}$) and its relatively high power consumption make its industrial applications still rare.

9.5 ADSORPTION

Adsorption refers to the ability of certain materials to retain molecules (gas, metallic ions, organic molecules, etc.) on their surface in a more or less reversible manner. There is a mass transfer of sorbate from the bulk of liquid or gas phase to the surface of the solid. The solid sorbent thus acquires superficial (hydrophobic or hydrophilic) properties liable to modify the state of equilibrium of the medium (diffusion, flocculation) [37].

The adsorptive capacity of the solid depends on [38]:

- The developed surface area or specific surface area of the material. Natural adsorbents (clays, silica, etc.) possess specific surface areas that vary with the physico-chemical state of the liquid medium (pH value, nature of the bound cations, surface saturation by organic molecules, etc.). Thus, certain clays such as bentonites (montmorillonite for instance) have a surface area that is accessible to most molecules and ranges from 40 to 800 $m^2 g^{-1}$. Their adsorptive capacity is quite variable but constitutes the main parameter in the regulation of transfers and in the mobility of elements in the natural environment. Industrial adsorbents (mainly activated carbon) can feature extensive surface areas (roughly between 600 and 1,200 $m^2 g^{-1}$) that are characteristic of a very strong microporosity. Other adsorbents such as metallic hydroxides that are formed in the course of the coagulation–flocculation process also develop very large surface areas whose expanse is closely dependent on the pH value.

– The nature of the adsorbate–adsorbent bond, in other words, on the free energy of interaction (G) between the adsorption sites and that part of the molecule which is in contact with the surface. This energy is directly measurable in the case of gas adsorption. However, in a liquid medium, the calorimetric methods only record the differential enthalpy of adsorption that corresponds to the difference between the adsorption energy of adsorbed molecules and the desorption energy of bound water at the interface.

– The contact time between the solid and the solutes. At equilibrium, there is a dynamic exchange between the molecules of the adsorbed phase and those that remain in solution. Many theories have attempted to model the relation that exists between the number of molecules adsorbed ($g\,g^{-1}$, $g\,m^{-2}$, etc.) and the number at equilibrium. One of the most commonly employed theories in the field of adsorption on activated carbon is reflected in the Freundlich equation [39] (Equation 9.5) depicted in Figure 9.18:

$$\frac{X}{m} = K\,C_{\text{eq}}^{1/n}, \tag{9.5}$$

where X/m is the weight of pollutant retained per unit weight of the adsorbent, and C_{eq} is the equilibrium concentration of pollutant molecules in the aqueous phase. K and n are energy constants depending on the adsorbate–adsorbent couple at a given temperature, which is kept constant during the operation (isotherm).

In fact, hardly any modeling, no matter how "complex," can adequately reflect the structure of the isotherm, and a fortiori explain the mechanisms of adsorption. The basic reason for this is that any surface is heterogeneous both as regards physical aspects and energy.

It is mainly the Van der Waals-type attraction and the Coulomb electrostatic-type attraction that provided the basis for adsorption that is ultimately based in thermodynamics and reflected in the resulting affinity between the sorbate moiety and the sorption active site. For instance, it can be seen

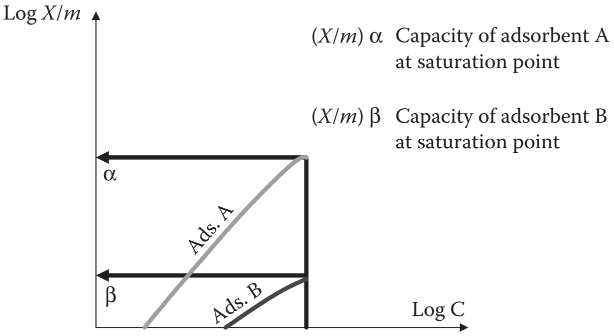

FIGURE 9.18 Freundlich isotherms.

that there is a strong affinity of aromatic molecules for the graphitic structure of carbon and a repulsion of the nonaromatic polar molecules.

9.5.1 MAIN ADSORBENTS

9.5.1.1 Activated Carbon

Experience shows that activated carbon has a broad spectrum of adsorptive activity, as most organic molecules are retained on its surface. The hardest to retain are the molecules that are the most polar and the linear ones with a very low molecular weight (simple alcohols, primary organic acids, etc.) [40]. Molecules that are slightly polar, generating taste and smell, and molecules with a relatively high molecular weight are for various reasons well adsorbed on carbon. It is interesting to note that, apart from these adsorbent properties, activated carbon can also provide a fine solid support for the growth of bacteria that are capable of breaking down a fraction of the adsorbed phase. In this combination, a part of the support is continuously being regenerated and capable of freeing sites, allowing new molecules to be retained. This combined action has successfully been used to enhance purification of certain types of wastewaters.

Activated carbon is available in two forms: powdered carbon and granular carbon. Powdered activated carbon (PAC) takes the form of grains between 10 and 50 mg and its use is generally combined with a clarification treatment. If it is added continuously to the water together with flocculating reagents, it enters the floc and is then extracted from the water with it. The PAC is about 2–3 times less expensive than granular activated carbon (GAC). The investment costs are low when the treatment involves only a flocculation/settling stage (an activated carbon feeder is all that is needed).

The physical characteristics of GAC vary considerably depending on the raw materials used to prepare the GAC (Table 9.8).

9.5.1.1.1 Main Applications

Activated carbon is used

- In the polishing treatment of drinking water or very pure industrial process water. In this case, the activated carbon will retain the dissolved organic compounds not broken down by natural biological means (self-purification of waterways): micropollutants and substances determining the taste and flavor of the water. The carbon will also adsorb traces of certain heavy metals.

TABLE 9.8
Physical Characteristics of GAC

Raw Material	**Peat, Wood, Coconut, Anthracite, . . .**
Form	Crushed, extruded
Grain size ES (mm)	0.25–3
UC	1.4–2.2
Friability 750 strokes (%)	10–50
1500 strokes (%)	20–100
Bulk density (compacted)	0.25–0.55
Specific surface area ($m^2 g^{-1}$)	500–1300
Ash content (%)	4–12

Note: ES: effective size.

- In the treatment of industrial wastewater, when the effluent is not biodegradable or when it contains certain organic toxic elements [41,42] that rule out the use of biological techniques. In this case, the use of activated carbon often allows the selective retention of toxic elements and the resultant liquid can thus be degraded by normal biological means.
- In the "tertiary" treatment of municipal and industrial wastewater. The carbon retains dissolved organic compounds that have resisted upstream biological treatment, and thus removes a large part of the residual COD.

9.5.1.1.2 Adsorptive Capacity of Carbon

GAC is used as a filter bed through which the water to be treated passes, leaving behind its impurities that are thus extracted methodically: the water, as it progressively loses its pollutants, encounters zones of activated carbon that are less and less saturated and therefore more and more active. Whether treatment using activated carbon is economical or not largely depends on the adsorptive capacity of the carbon, expressed in grams of retained COD per kilogram (or volume) of activated carbon, which characterizes the "carbon requirements" for a given result [43]. For a given polluted water–carbon system, this capacity depends on [44,45]

- *The depth of the bed:* The deeper the bed, the easier it deals with extended adsorptive fronts inside the bed without excessive breakthrough leakage—while still ensuring thorough saturation of the upper layers.
- *The exchange rate:* The experience shows that three volumes of water per volume of carbon per hour can seldom be exceeded when treating high levels of pollution. In the case of drinking water, in which the content of adsorbable products is very low, any decision as to the economic optimum has to take the high investment costs into account, with the result that higher bed volumes are used: $5–10\,\mathrm{vol\,vol^{-1}\,h^{-1}}$, with a smaller degree of carbon saturation.

The theory only gives an indication of the trend of the laws of adsorption. It still remains indispensable to call upon the experience of the expert and to carry out dynamic tests on columns of sufficient size so that results can be extrapolated.

A compact bed has four functions:

- *Filtration:* This must often be reduced to a minimum in order to avoid clogging of the bed which is unavoidable without efficient washing systems to break up the layers completely after each cycle. In addition, the carbon tends to extract adsorbable products from the floc with which it is in contact, causing premature saturation. That is why it is often advisable to use sand filtration as a preliminary clean-up step to remove suspended matter particles.
- *Medium for supporting microbial growth:* This phenomenon can contribute to the process of purification, but can also be very dangerous if not properly controlled (anaerobic fermentation gives off odors, clogging of the bed, etc.).
- *Adsorption:* This must remain the basic role of the carbon.

There are three possible arrangements:

- *Simple fixed beds*: This technique is widely used in drinking water treatment.
- *Fixed beds in series*: A series of several columns, which are regenerated by permutation, are used (Figure 9.19). Thus, a countercurrent extraction system is organized.
- *Moving beds*: These usually make use of the countercurrent principle (Figure 9.20). The base of the bed can even be fluidized.

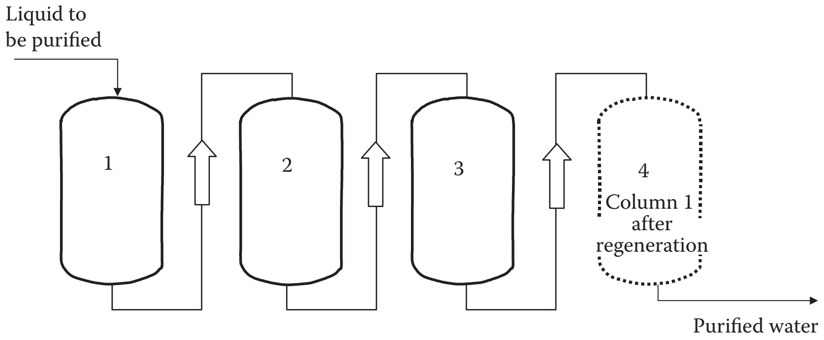

FIGURE 9.19 Diagram of fixed bed in series.

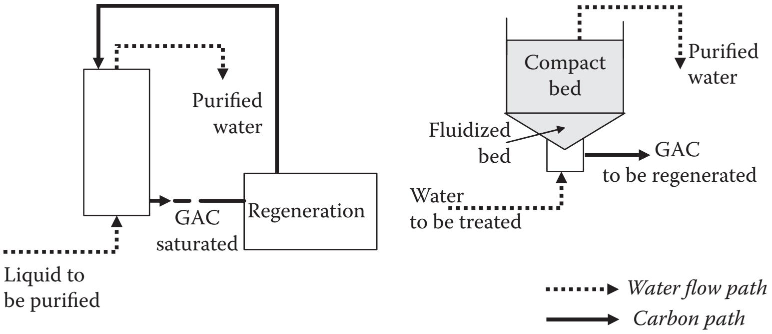

FIGURE 9.20 Diagrams of moving beds.

9.5.1.1.3 Regeneration of the Activated Carbon

Activated carbon (such as artificial adsorbents) is an expensive product. In most cases the cost of replacing the saturated carbon would be prohibitive [46]. It should therefore be regenerated, and three methods have been developed for this purpose:

- *Steam regeneration:* This method is restricted to regenerating carbon which has only retained a few very volatile products. However, steam treatment can be useful in unclogging the surface of the grains and disinfecting the carbon.
- *Thermal regeneration:* By pyrolysis and burning off of adsorbed organic substances. To avoid igniting the carbon, it is heated to about 800°C in a controlled anoxic atmosphere. This is the most widely used method and regenerates the carbon very well, but it has two disadvantages: (1) It requires considerable investment in either a multiple-hearth furnace, a fluidized bed furnace, or a rotary kiln. The furnace must have monitoring devices for its gaseous atmosphere and temperature, a dewatering system at the inlet, and a carbon quenching system at the outlet. (2) It causes high carbon losses (7–10% per regeneration), so that after 10–14 regenerations, the GAC volume will, on average, have been entirely replaced. The use of electrical heating (infrared furnace, induction furnace) reduces these losses. However, these methods, which are expensive, are only used for the recovery of costly metals.
- *Chemical regeneration:* The advantage of this process is that for the same capital outlay, only minimum carbon loss occurs (about 1% of the quantity treated). However, the use of chemical reagents for regeneration (alkaline reagents, solvents) leads to the formation of eluates from which the solvent must be separated by distillation. The pollutants are then destroyed by incineration unless they can be recovered. The process is less widely used than thermal regeneration.

- *Biological regeneration:* This method of regeneration is somewhat complicated due to the necessity of controlling the microbial action and thus it is rarely applied on an industrial scale.

9.5.1.2 Other Adsorbents

Apart from the activated carbon, new adsorbents have been developed:

- *Inorganic adsorbents:* Alumina [47,48] and other metallic oxides [49]: they can have a very large specific surface area, but these solids adsorb more selectively than carbon. Their capacity depends very much on the pH value and their mesoporosity. Below the isoelectric point only negatively charged molecules are adsorbed on positively charge sites. In the current state of their development, these adsorbents are not competitive with activated carbon. However, some of these solids such as the alumina or the ferric oxyhydroxides have the advantage of removing arsenic, fluoride, phosphates, nitrates, and so on.
- *Organic adsorbents:* Macromolecular resins with specific surface areas of between 300 and 750 $m^2 g^{-1}$ [50,51]: their adsorptive capacity is generally lower when compared with that of activated carbon. However, these resins can have special adsorptive properties and are often easier to regenerate (low binding energy). Here the "scavengers" should also be mentioned, which are highly porous anionic resins. However, these resins have a smaller specific surface area and their action on polar substances (such as humic acids and anionic detergents) is partly due to their ionic charge, which distinguishes them from other adsorbents.

9.6 OXIDATION–REDUCTION

Some substances are found either in oxidized or in reduced form, and are converted from one to the other by gaining electrons (reduction) or by losing electrons (oxidation). A system comprising an acceptor and a donor of electrons is known as an "oxidation–reduction" system.

Oxidation–reduction reactions are used in the treatment of water for disinfection and to convert an element from its dissolved state to a state in which it may be precipitated (Fe, Mn, sulfur removal, etc.) [52].

The definition and monitoring of the pH value in a reaction is very important. Eh–pH diagrams exist in handbooks to represent the state of various forms of elements and their evolution depending on the pH and the redox potential, in order to

- Convert an element from its dissolved state to its gaseous state (e.g., denitrification)
- Break down a substance into several simpler substances, the presence of which is acceptable in water (e.g., phenols, etc.)
- Break down a nonbiodegradable substance into several simpler substances, which can be removed by bacterial assimilation during a later treatment phase (e.g., micropollutants).

Oxidation can take place by means of chemotrophic bacteria such as in the oxidation of iron and manganese, the oxidation of sulfur compounds, the oxidation–reduction of nitrogen compounds, and methane-forming reduction [53–56].

9.6.1 MAIN OXIDATION TECHNIQUES

This mainly concerns the following industrial waters and effluents:

Using oxidizing reagents:

- Cyanide-laden waters from electroplating or gas scrubbing
- Hydrazine-laden condensates: oxidation by H_2O_2 catalyzed on specific resins

- Nitrite baths from electroplating: oxidation by $H_2O_2 + Cu^{2+}$ (Fenton reagent), NaClO, or H_2SO_5
- Solutions of thiosulfates oxidizable from H_2O_2.

Using air or oxygen [23,57]:

- Spent caustic soda, rich in S^{2-}
- Waters from pickling, loaded with Fe^{2+}
- Uranium leachates U^{4+}.

Most of these reactions present a high enough potential and rapid enough kinetics to permit regulation except in the case of thiosulfates. If other less dangerous reducing agents coexist, a posteriori monitoring to limit the over consumption of a costly oxidizing agent, as in the case of cyanide-laden effluents from gas scrubbing, is considered adequate. The use of air and oxygen in the equipment known as "oxidizers" requires high temperatures and pressures in order to achieve adequate kinetics and efficiency.

Ozone can also be used for oxidation reactions, especially for

- Effluents containing low CN or phenol concentrations
- Effluents from methionine units or those containing refractory compounds.

9.6.1.1 Application: Treatment of Cyanides

The oxidation of cyanides in an alkaline environment theoretically comprises two successive stages. The first one, in which there is practically no toxicity, is the cyanate state and then the nitrogen and bicarbonate state. Powerful oxidizing agents employed are sodium hypochlorite, chlorine, and permonosulfuric acid (Caro's acid). In practice, for economic reasons, only the first stage is employed.

First stage (cyanates):

The overall reactions that come into play are

- Using sodium hypochlorite: $NaCN + NaClO \Leftrightarrow NaCNO + NaCl$
- Using chlorine gas: $NaCN + C1_2 + 2NaOH \Leftrightarrow NaCNO + 2NaCl + H_2O$
- Using Caro's acid: $NaCN + H_2SO_5 \Leftrightarrow NaCNO + H_2SO_4$.

The first two reactions occur almost instantaneously when the pH level is above 12, but the reaction speed drops rapidly if the pH level falls (critical threshold: pH 10.5). Whatever the pH level, an intermediate compound that is formed is cyanogen chloride CNCI, which is just as dangerous as hydrocyanic acid:

$$NaCN + NaClO + H_2O \Leftrightarrow CNCI + 2NaOH.$$

With a pH level starting at 10.5, however, cyanogen chloride is hydrolyzed the moment it is formed according to the reaction:

$$CNCI + 2NaOH \Leftrightarrow NaCl + NaCNO + H_2O.$$

With Caro's acid, an adequate reaction speed is observed for pH level above 9.5.

Second stage (nitrogen):

The breakdown of cyanate into nitrogen occurs according to the reaction:

$$2NaCNO + 3C1_2 + 6NaOH \Leftrightarrow 2NaHCO_3 + N_2 + 6NaCl + 2H_2O.$$

It also takes place at the pH level of 12, but requires three times the amount of reagent and a reaction time of about 1 h as it is impossible to regulate the potential.

9.6.2 MAIN REDUCTION TECHNIQUES

The most common examples involve the reduction of oxygen, that of hexavalent chromium [58], as well as the destruction of residual oxidizing agents employed in disinfection. It is also necessary to mention the reduction of nitrites in the process of surface treatment (sulfamic acid or $NaHSO_3$).

9.6.2.1 Application: Reduction of Hexavalent Chromium

The reduction of toxic hexavalent chromium into trivalent chromium which is less toxic and can be precipitated in the form of hydroxide occurs in an acid medium through the action of sodium bisulfate or ferrous sulfite.

Using sodium bisulfite:

$$H_2Cr_2O_7 + 3NaHSO_3 + 3H_2SO_4 \Leftrightarrow Cr_2(SO_4)_3 + 3NaHSO_4 + 4H_2O.$$

Using ferrous sulfate:

$$H_2Cr_2O_7 + 6FeSO_4 + 6H_2SO_4 \Leftrightarrow Cr_2(SO_4)_3 + 3Fe_2(SO_4)_3 + 7H_2O.$$

The first of these reactions occurs almost instantaneously when the pH level is below 2.5, but the reaction speed falls rapidly when the pH level rises (the critical threshold is at pH 3.5).

The reduction of ferrous iron has fewer restrictions and may occur with a pH level below 6, with monitoring. It is less used because a significant amount of hydroxide sludge is produced during the final neutralization stage.

9.7 LIQUID–LIQUID EXTRACTION

The liquid–liquid extraction process is a basic operation that allows a component (solute) to be extracted from an inert liquid by another liquid known as a solvent [59]. The liquid phase 1 is a homogeneous mixture. The solvent must not be miscible with one of the two initial compounds. The inert compound and the solvent are usually not miscible. Liquid–liquid extraction is also governed by the laws of mass transfer and it is necessary to determine features that favour exchange, such as maximum interfacial area, wide concentration difference, and a notable transfer (or extraction) coefficient. There are two main types of industrial equipment employed in the liquid–liquid extraction process [60]:

- Contactors with several separate stages in series. At each stage, the functions of dispersion followed by separation of the two phases take place in two successive units: the mixing-settling tank and the hydrocyclone-settling tank.
- Differential contactors in which one phase is dispersed into the other on a countercurrent basis. Following this, the phases are separated in the two ends of a vertical column (Figure 9.21). The method of dispersion of the two phases may be by gravity, mechanical stirring, pulsation, etc. Spinning mechanical countercurrent contactors (Podbielniak) proved to be extremely efficient—for the price and elevated energy consumption.

Liquid–liquid extraction is used for phenol removal [61] from spent caustic soda from refineries using gas oil as a solvent. The efficiency of phenol removal reported was high (90–95%) when pulsed columns with perforated trays were used.

9.8 WETLAND METAL MINERALIZATION

A broadly accepted definition of a wetland is "an area that meets one or more of the following conditions: (1) areas supporting predominately hydrophytes, (2) areas with predominately undrained hydritic soil producing anaerobic conditions, and (3) areas with a nonsoil substrate" [62]. Figure 9.22 pictures a constructed wetland (CW). Wetlands are also ephemeral in that they depend on

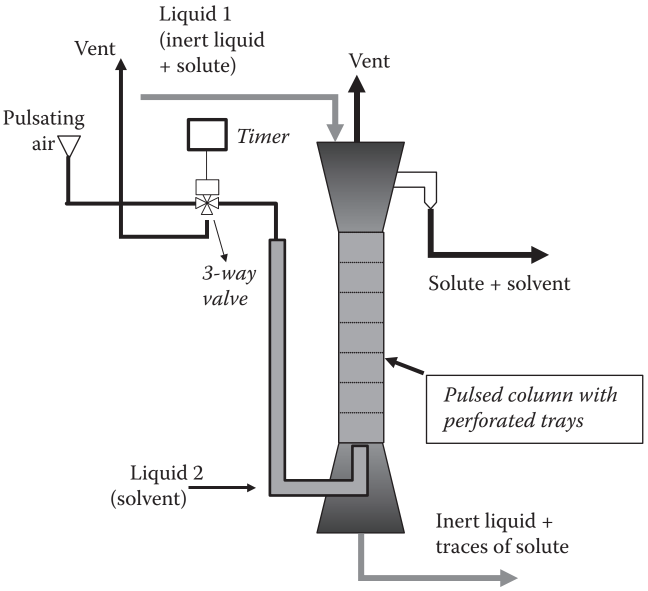

FIGURE 9.21 Diagram of a pulsed column liquid–liquid extraction.

perturbations to their environment in order to exist [63]. Without these disturbances, wetlands will eventually dry up and become stable soil substrate for other terrestrial ecosystems. It is this dynamic property of wetlands that makes them suitable for the treatment of polluted wastewaters because they have the capacity to absorb and smooth variations in hydrological input and reduce substantial concentrations of pollutants. Wetlands have also shown incredible tolerance to metals [64,65] and their ability to accumulate metals such as iron and manganese has been known for centuries. There

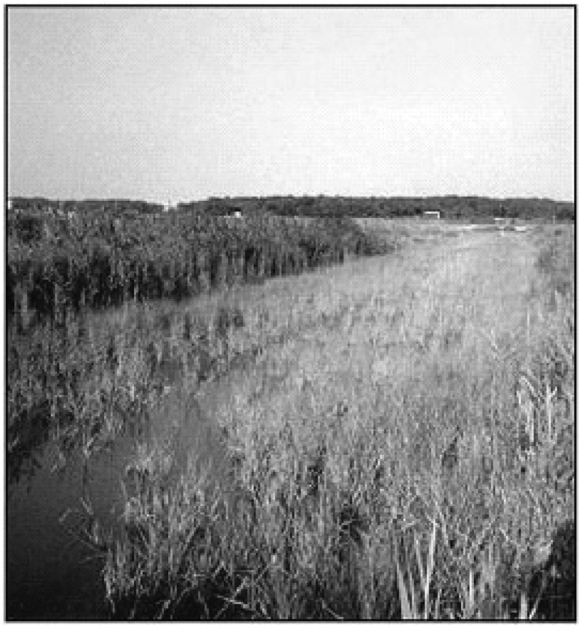

FIGURE 9.22 A constructed wetland.

are generally two types of CWs: (1) free water surface (FWS) and (2) subsurface flow (also referred to as vegetated submerged bed types, root zone method, microbial rock filters, and hydrobotanical systems). In engineering terms, both can be referred to as attached growth biological reactors. The FWS wetlands are constructed so that an exposed area of water will always exist, and also so that mixing will lead to oxygenation of the surface sediments. These wetlands have the disadvantage that they usually require some form of primary treatment to their influent waters [66]. The subsurface flow wetlands (SFW) are the most common for treating metal-rich wastewaters. They are designed with an organic, porous medium and gradual slope so that no FWS exists, and so that the saturated conditions and organic matter decomposition lead to anoxic sediments. The lack of a FWS also has the advantage of avoiding odor and insect vector problems. If effluent acidity is a problem (as it **Q1** always is in AMD and can sometimes be for industrial processes), then the SFW is very advantageous because it can be underlain with crushed limestone which, under the anoxic conditions, can slowly release alkalinity without becoming armored by metal precipitate coatings which would otherwise occur under oxic conditions [67]. Furthermore, SFWs are also advantageous compared with FWSs because they usually require less preliminary treatment [66].

9.8.1 ELEMENTS OF DESIGN

CWs are attempts at replicating and optimizing natural ecosystems. They are essentially systems that incorporate microbial, planktonic, invertebrate, soil, and hydrophytic components into a dynamic ecosystem [68,69]. For the purpose of CWs though, designers are usually only interested in three components: (1) vegetation; (2) microbes, algae, and microbially mediated processes; and (3) substrate conditions.

9.8.2 VEGETATION

Many plant species have been used in CWs. These include (most common to least) *Typha latifolia* (cattails), *Scirpus validus*, *Scirpus robustus* (bulrush), *Phragmites communis* (common reed), *Leersia oryzoides* (cutgrass), and *Lemna minor* (duckweed). Plants in CWs generally play two roles: (1) their roots provide increased surface area for the attachment of microbes and epiphytes, and (2) by their hydrophytic nature, wetland plants have the capability to transport oxygen down into their roots where some leakage occurs through radial oxygen loss, thus oxygenating the surrounding anoxic substrate. Although it may seem deceiving due to their dominant presence in wetlands, the plants themselves only account for at most ~1% of the total heavy metal removal via uptake [70]. Most of this removal occurs in the plant root tips, which is not advantageous if plant harvesting is a desired method for permanent metal removal, as roots remain in the substrate after harvesting. Another important function of emergent plants is that they accelerate the establishment of the necessary microbial population to less than a year, compared with almost two years without vegetation [71]. The most important role of emergent vegetation in the CW is their ability to transport oxygen into the anoxic sediment. This function is necessary to support aerobic microorganisms and remove dissolved metals through oxidization. Transport results from thermoosmosis of gases that requires a special plant morphological structure called aerenchyma, but does not actually require physiological activities. The oxygen-transporting capabilities of wetland plants vary among species. Studies have shown that *Typha* can transport the most with mixed assemblages following in the sequence [72]:

Q2 *Typha latofolia* > *J. effuses* > *S. americanum or S. cyprinus* > *E. quadranguilata*.

Not only do *Typha* exhibit the greatest capacity to transport oxygen, but they also concentrate most metals in their roots. Meiorin et al. [73] found *Typha* to accumulate 447–1,220 $\mathrm{mg\,kg^{-1}}$ dry weight of Mn in much larger concentrations than other species studied. Furthermore, the rhizospheres of *Typha* were found to be extremely conducive environments for aerobic heterotrophs such as *Thiobacillus* [74], which are essential for metal removal. Overall then, the literature indicates that *Typha* species might be the most appropriate wetland plants for heavy metal removal.

Some studies have also focused on the metal removal by *Sphagnum* species which, at times, can be substantial [65]. However, since the removal capacities of this plant are directly linked to its cation exchange capacity [75], which eventually becomes saturated [76], and *Sphagnum* species have a very low net productivity and so are dependent on outside sources for nutrients [75], their use in CWs does not promise sustainable heavy metal removal.

9.8.3 Algae, Microbes, and Microbially Mediated Processes

Algae and microbes are by far the most abundant living organisms in a wetland. The microbial population can sometimes reach $10^{10}\,\mathrm{mL}^{-1}$ in organic sediments that are ubiquitous in wetland ecosystems [77]. The processes by which algae remove metals are bioaccumulation, biosorption, and either aerobic or anaerobic biologically mediated deposition by mineralization. The capacity of microbes and algae to sequester heavy metals or to cause their removal from solution is measured not only by the percent of metals retained, but also by the bioavailability of these metals in the marsh system after being removed from solution. Therefore, the ideal mechanism for heavy metal removal would be one where the removed metal could not re-enter the solution phase or the biota.

The metal accumulation capacity of certain algae is a remarkable phenomenon in nature. Their ability to sequester metals from solution was first noticed in the early 1970s when it was observed that lagoon effluents from lead/zinc mining and milling operations were causing dense mat-like growths of algae in receiving streams [78]. These algal growths were irregularly dense partly because the receiving waters were so polluted with heavy metals that the normal competitors of algae were practically eliminated.

The microbially mediated reactions can be broken down into those that occur in aerobic sediments and those that occur in anaerobic sediments. In aerobic regions, heterotrophic microbes such as *Arthrobacter*, *Pseudomonas*, and *Citrobacter* can mediate the following reaction [79]:

$$2\mathrm{MnSO_4} + \mathrm{O_2} + 2\mathrm{H_2O} \Leftrightarrow 2\mathrm{MnO_2} + 2\mathrm{H_2SO_4},$$

whereas *Metallogenium* mediates another reaction:

$$2\mathrm{MnSO_4} + \mathrm{H_2O_2} \Leftrightarrow \mathrm{MnO_2} + \mathrm{H_2SO_4}.$$

The overall effect is the precipitation of the insoluble Mn oxide into the sediments where it will hopefully remain. Another metal removal reaction results from the microbial decay of organic matter that promotes the formation of NH_3 and HCO_3^-, which increase the pH and cause hydroxide and Mn and Fe oxyhydroxide formation and consequent precipitation in aerobic zones [80]. These microbially mediated reactions are further enhanced by the fact that other dissolved metals adsorb onto the metal oxyhydroxides and are also precipitated from solution. In the latter adsorption reaction, Mn oxyhydroxides are more important than Fe oxyhydroxides [80] and there are many different bacteria that can oxidize Mn [77], making the removal of Mn by this process very important. Moreover, the formation of oxyhydroxides, especially those of Al [81], is not favored under acidic conditions, which also emphasizes the importance of the buffering limestone underlayer of SFWs to this oxidation reaction. Finally, Giblin et al. [82] found that Fe, Pb, and Mn were trapped in the sediments in a form that was unavailable for reuptake into the biota or resuspension back into solution, so these metals are, for the most part, permanently removed by the above processes.

In SFWs, the most important microbially mediated process to remove heavy metals is the anaerobic formation of H_2S. In anoxic regions, bacteria such as *Desulfovibrio* oxidize organic matter using sulfate as the electron acceptor and reducing it to H_2S. Some of the important chemical reactions include [69]:

Sulfate reduction: $SO_4^{2-} + 2CH_2O \Leftrightarrow H_2S + 2HCO_3^-$
Iron monosulfate formation: $Fe^{2+} + HS^- \Rightarrow FeS + H^+$

Pyrite formation: $FeS + S^0 => FeS_2$
Pyrite formation: $Fe^{2+} + H_2S + S^0 => FeS_2 + 2H^+$
Pyrite formation: $Fe^{2+} + HS^- + S_x^{2-} => FeS_2 + S_x^{2-} + H^+$.

The formation of pyrite is better than Fe oxyhydroxides because pyrite accumulates within the organic substrates and is less likely to form surface deposits or be washed out during storm events [69]. Two of the biggest advantages of sulfate reduction are that it produces alkalinity and also that it is not constrained by accumulation limits or toxic effects. Pyrite is also negligibly soluble in acid of neutral water, so the formation of this mineral represents a long-term, sustainable mechanism for removing Fe from solution. However, the importance of sulfate reduction in heavy metal removal depends on the availability of sulfate in the influent waters and also on the type of metal sulfide complexes formed. The latter issue is unclear in the literature as Fe sulfides are the only complexes that have been extensively studied, whereas other metal complexes have been mentioned but their formation mechanisms were not included.

9.8.4 SUBSTRATE CONDITIONS

Many different substrates have been used in CWs. The overall goal of the substrate in an SFW is to provide nutrients and support for vegetation, while at the same time it must be porous so as not to inhibit lateral hydrological flow. The substrate can also have certain functions in metal removal because of its sorption properties. The best-known example of this is the use of *Sphagnum* as a substrate [65,75]. However, the performance of *Sphagnum* is limited because it does not have a very high nutrient status and because its sorption sites eventually become saturated. Another study, which investigated the sorption of Pb onto particles [83], reported that the amount of organic matter in the particles was the key factor limiting sorption. Therefore, it appears that the most appropriate substrate for metal removal in CWs requires a high percent of organic matter content. This is advantageous because wetlands themselves can contribute up to 67% of their annual net primary productivity to the sediments [70], replacing thus consumed sorption sites. The most frequently used substrate for treating AMD has been mushroom compost, which has a very high organic matter content (1–3%), combined with crushed limestone. Mushroom compost is a byproduct of the mushroom-growing industry and is formed by the anaerobic composting of a mixture of hay, manure, and agricultural wastes. Brodie et al. [71] evaluated the performance of several substrates but did not include mushroom compost. They found that there were no significant differences between the metal removal efficiencies of different substrates (soils included natural wetland, acid wetland, clay, mine spoil, and pea gravel). Except for the two natural wetland soils, none of the substrates investigated by Brodie et al. [71] could be used for long-term projects because of their low nutrient status. Furthermore, these results were difficult to interpret due to inconsistent experimental hydrologic flow rates. Therefore, further work regarding the effect of substrate type on metal removal should consider more commonly used substrates, especially mushroom compost.

9.8.5 METAL REMOVAL EFFICIENCIES

There are many publications that cite metal removal efficiencies of wetlands (Table 9.9). Unfortunately, these citations cannot contribute to further understanding of the complex process of heavy metal removal because very few concurrently give information on the respective wetland parameters. The removal efficiencies for the wetlands studied here range from 100% for Fe, Cu, or Pb to 0.6% for Cd.

The relevant literature [71,74,84,85] seems to agree that in terms of substrate and plant species selection, high organic matter is important in the substrate and that *Typha* species are associated with high metal removal rates. Furthermore, the metal removal efficiencies decrease with increasing

TABLE 9.9
Heavy Metal Removal Efficiencies of Various Wetlands and Cws From the Literature

	Removal Efficiency (%)								
References	**Cd**	**Cr**	**Cu**	**Pb**	**Hg**	**Zn**	**Fe**	**Mn**	**Ni**
[99]	50–90	50–90	50–90	80–95	50–90	50–90			
[82]	20–35	20–50	60–100	55–100		20–45	60–100	55–60	
[73]		40–53	5–32	30–83		6–51			12–32
[100]			99	94		98	86		
[80]			92						84
[80]	0.3		14			5.8	70	0.7	

Note: The removal efficiencies for each metal (calculation of removal efficiency assumed to be $((([in] - [out])/[in])*100\%)$.

flushing rate, wetland depth, and for some metals, with wetland area, experiment duration, and temperature. On the other hand, Mn removal increased with longer experiment durations. Some other wetland characteristics that are important to metal removal are length-to-width ratio, which increases with increasing Fe removal, and limestone, which also significantly improved Fe removal. The results also suggest that costs can be reduced by building shallower wetlands with natural substrate conditions (except for a little limestone). These financial implications might also enhance the capabilities of CWs as a low-tech alternative to heavy metal abatement of wastewaters.

9.9 BIOSORPTION

Metal accumulation has been demonstrated in a significant number of microorganisms (bacteria, algae, yeasts, and fungi) and this phenomenon is associated with a wide spectrum of microbial activities. Leaving aside the metabolically mediated metal sequestration by living microbial cells (*bioaccumulation*), which has been studied particularly from toxicological point of view, it has been observed that some microbial cells tend to bind metals even when they are dead and metabolically nonactive (Table 9.10). This type of metal uptake, termed *biosorption*, is usually rapid and sometimes very high, which makes it particularly interesting from the application point of view [86]. The metals may be bound in the biomass through a variety of mechanisms: adsorption, ion exchange, coordination, complexation, chelation, and microprecipitation seem to occur to a varying degree [87,30].

The metal-binding chemical groups of the biological materials include carboxylate, phosphate, hydroxyl, sulfhydryl, and amines, present in durable and decomposition-resistant cell walls [88,89].

TABLE 9.10
Metal-Binding Capacities of Selected Biomass

Biomass Species	**Biosorbent Capacity** (m eq g^{-1})	**References**
Sargassum natans	2–2.3	[101]
Ascophyllum nodosum	2–2.5	[101]
Rhizopus arrhizus	1.1	[87]
Eclonia radiata	1.8–2.4	[102]
Peat moss	4.5–5	[103]
Commercial resins	0.35–5	[104]

The pH of the metal-bearing solution can play a critical role in influencing the metal-sequestering ability of the biomass materials [90–92].

Earlier patents awarded for the application of biomaterials in metal concentration indicate the technological potential of the biosorption phenomenon [93–95]. The packed-bed contacting column appears to be the most effective mode of bringing together the metal-bearing solution and biosobent material [96]. Most often it is possible to wash the resulting metal-saturated biosorbent in the same column, releasing the deposited metal in a small volume of "desorption" solution which then contains the metal in high concentrations [30,97,98]. This makes the subsequent recovery of the metal possible by routine commercial methods (e.g., electrowinning). The regenerated biosorbent can be then used in many sequential metal sorption cycles. Multiple uptake desorption cycles further decrease already quite cost-effective potential of the biosorption process, making its applications economically very attractive. The recently published book on *Sorption and Biosorption* [30] summarizes the current knowledge in the field of biosorption.

REFERENCES

1. Droste, R. L. *Theory and Practice of Water and Wastewater Treatment*, p. 789. Wiley, 1995. Q3
2. Metcalf and Eddy, Inc. *Wastewater Engineering—Collection, Treatment, Disposal*, p. 444. McGraw-Hill, New York, 1972.
3. ACG Technology Ltd. *Heavy Metals Removal and Recovery*, p. 12. Industrial Process Products and Technology, 1989. Q4
4. US Environmental Protection Agency (US EPA). Processes, procedures and methods to control pollution from mining Activities. US EPA # 430/9-73-011, 1973.
5. Eckenfelder, W. W. *Activated Sludge Treatment of Industrial Wastewater*, p. 281. Technomic Publishing Co., 1995.
6. Viessman, W. J. and Hammer, M. J. *Water Supply and Pollution Control*, p. 888. Prentice-Hall, 2004.
7. Noble, R. D. and Stern, S. A. *Membrane Separations Technology—Principles and Applications*, p. 718. Elsevier, Amsterdam, 1995.
8. Albertson, O. E. *Dewatering Municipal Wastewater Sludge*, p. 189. Noyes Data Corporation/Noyes Publications, 1991.
9. Andreoli, C. V., Von Sperling, M., and Fernandes, F. *Sludge Treatment and Disposal*, p. 244. IWA Publishing, 2007.
10. Bishop, P. *Municipal Sewage Sludge Management: Processing, Utilization and Disposal*, p. 659. Technomic Publishing Company, Inc., Lancaster, PA, 1992.
11. Krishnan, E. R., Utrecht, P. W., Patkar, A. N., Davis, J. S., Pour, S. G., and Foerst, M. E. *Recovery of Metals from Sludges and Wastewaters*, p. 138. Noyes Data Corporation, Park Ridge, NJ, 1993.
12. Blais, J. F. and Tyagi, R. D. Comparison of acid and microbial leaching for metal removal from municipal sludge. *Water Sci. Technol.*, 26(1–2), 197–206, 1992.
13. Sreekrishnan, T. R., Blais, J. F., and Tyagi, R. D. Kinetics of heavy metal bioleaching from sewage sludge. *Water Res.*, 27(11), 1641–1651, 1993.
14. Dobson, R. S. and Burgess, J. E. Biological treatment of precious metal refinery wastewater: A review. *Miner. Eng.*, 20(6), 519–532, 2007.
15. Loser, C., Zehnsdorf, A., Hoffmann, P., and Seidel, H. Remediation of heavy metal polluted sediment by suspension and solid-bed leaching: Estimate of metal removal efficiency. *Chemosphere*, 66(9), 1699–1705, 2007.
16. Chen, J. H. and Huang, C. E. Selective separation of Cu and Zn in the citric acid leachate of industrial printed wiring board sludge by D(2) EHPA-modified Amberlite XAD-4 resin. *Ind. Eng. Chem. Res.*, 46(22), 7231–7238, 2007.
17. Lee, I. H., Kuan, Y. C., and Chern, J. M. Factorial experimental design for recovering heavy metals from sludge with ion-exchange resin. *J. Hazard. Mater.*, 138(3), 549–559, 2006.
18. Sirianuntapiboon, S. and Hongsrisuwan, T. Removal of Zn^{2+} and Cu^{2+} by a sequencing batch reactor (SBR) system. *Bioresour. Technol.*, 98(4), 808–818, 2007.
19. Turek, M., Korolewicz, T., and Ciba, J. Removal of heavy metals from sewage sludge used as soil fertilizer. *Soil Sediment. Contam.*, 14(2), 143–154, 2005.
20. Vandevivere, P., Hammes, F., Verstraete, W., Feijtel, T., and Schowanek, D. Metal decontamination of soil, sediment, and sewage sludge by means of transition metal chelant S,S-EDDS. *J. Environ. Eng.—ASCE*, 127(9), 802–811, 2001.

21. Blais, J. F., Meunier, N., Mercier, G., Drogui, P., and Tyagi, R. D. Pilot plant study of simultaneous sewage sludge digestion and metal leaching. *J. Environ. Eng.—ASCE*, 130(5), 516–525, 2004.
22. Benmoussa, H., Tyagi, R. D., and Campbell, P. G. C. Simultaneous sewage sludge digestion and metal leaching using an internal loop reactor. *Water Res.*, 31(10), 2638–2654, 1997.
23. Filali-Meknassi, Y., Tyagi, R. D., and Narasiah, K. S. Simultaneous sewage sludge digestion and metal leaching: Effect of aeration. *Process Biochem.*, 36(3), 263–273, 2000.
24. Meunier, N., Tyagi, R. D., and Blais, J. F. Acid treatment for stabilization of sewage sludge. *Can. J. Civ. Eng.*, 23(1), 76–85, 1996.
25. Brooks, C. S. *Metal Recovery from Industrial Waste*. Lewis Publishers, Chelsea, MI, 1991.
26. Zagorodni, A. A. *Ion Exchange Materials: Properties and Applications*, p. 496. Elsevier Science & Technology Books, 2006.
27. Korkisch, J. *Handbook of Ion Exchange Resins: Their Application to Inorganic Analytical Chemistry*, p. 295. CRC Press, Boca Raton, FL, 1994.
28. Harland, C. E. *Ion Exchange: Theory and Practice*, p. 40. The Royal Society of Chemistry Cambridge, 1994.
29. Byrne, W. *Reverse Osmosis, a Practical Guide for Industrial Users*, p. 636. Tall Oaks Publishing Inc., 1995.
30. Volesky, B. *Sorption and Biosorption*. BV Sorbex, Inc., www.biosorption.com/order, Montreal, Canada, 2003.
31. Kim, B. M. and Weininger, J. L. Electrolytic removal of heavy metals from wastewaters. Elimination of end-of-the-line treatment is the key to important savings of capital and operating costs. *Envion. Prog.*, 1(2), 121–125, 2006.
32. Wang, J. Y., Zhang, D. S., Stabnikova, O., and Tay, J. H. Evaluation of electrokinetic removal of heavy metals from sewage sludge. *J. Hazard. Mater.*, 124(1–3), 139–146, 2005.
33. McLay Dedietrich, W. J. and Reinhard, F. P. Waste minimization and recovery technologies. *Metal Finishing*, 10, 715–742, 2007.
34. Simonsson, D. A flow-by packed-bed electrode for removal of metal ions from waste waters. *J. Appl. Electrochem.*, 15(5), 595–604, 2007.
35. Scott, K. A consideration of circulating bed electrodes for the recovery of metal from dilute solutions. *J. Appl. Electrochem.*, 18(4), 504–510, 1988.
36. Mohammadi, T., Razmi, A., and Sadrzadeh, M. Effect of operating parameters on Pb^{2+} separation from wastewater using electrodialysis. *Desalination*, 167(1–3), 379–385, 2004.
37. Dabrowski, A. *Adsorption and its Applications in Industry and Environmental Protection, Applications in Environmental Protection*, p. 1090. Elsevier Science, 1999.
38. Cheremisinoff, P. N. and Ellerbush, F. *Carbon Adsorption Handbook*, p. 251. Ann Arbor Science, Ann Arbor, MI, 1978.
39. Freundlich, H. *Colloid and Capillary Chemistry*. Methuen, London, 1926.
40. Bansal, R. C. and Goyal, M. *Activated Carbon Adsorption*, p. 495. CRC Press—Taylor & Francis Group, 2005.
41. Chen, J. P., Yiacoumi, S., and Blaydes, T. G. Equilibrium and kinetic studies of copper adsorption by activated carbon. *Sep. Tech.*, 6(2), 133–146, 1996.
42. Gabaldon, C., Marzal, P., Seco, A., and Gonzales, J. Cadmium and copper removal by a granular activated carbon in laboratory column systems. *Sep. Sci. Technol.*, 35(7), 1039–1053, 2000.
43. Marsh, H. and Reinoso, F. R. *Activated Carbon*, p. 525. Elsevier, 2006.
44. Chen, J. and Lin, M. S. Equilibrium and kinetic of metal ion adsorption onto a commercial H-type granular activated carbon: Experimental and modeling studies. *Water Res.*, 35(10), 2385–2394, 2001.
45. Netzer, A. and Hughes, D. E. Adsorption of copper, lead and cobalt by activated carbon. *Water Res.*, 18, 927–933, 1984.
46. Cole, P. M., Von Broembsen, D. S., and Laxen, P. A. A novel process for regeneration of carbon. In: Fivaz, C. E., Ed., *Proc. Gold 100 Conf.*, pp. 133–155. South Africa Inst. Min. Metall., Johannesburg, 1986.
47. Batista, J. R. and Young, J. C. Removal of selenium from gold heap leachate by activated alumina adsorption. *Min. Met. Proc.*, 14(2), 29–37, 1997.
48. Boddu, V. M., Abburi, K., Talbott, J. L., and Smith, E. D. Removal of hexavalent chromium from wastewater using a new composite chitosan biosorbent. *Environ. Sci. Technol.*, 37(19), 4449–4456, 2003.
49. Dzombak, D. A. and Morel, F. M. M. *Surface Complexation Modeling: Hydrous Ferric Oxide*, pp. 1–35. Wiley, New York, 1990.

50. Balaji, T. and Matsunaga, H. Adsorption characteristics of As(III) and As(V) with titanium dioxide loaded amberlite XAD-7 resin. *Analyt. Sci.*, 18(12), 1345–1349, 2002.
51. Els, E. R., Lorenzen, L., and Aldrich, C. The adsorption of precious metals and base metals on a quaternary ammonium group ion exchange resin. *Miner. Eng.*, 13(4), 401–414, 2000.
52. Holbein, B. E., DeVoe, I. W., Neirinck, L. G., Nathan, M. F., and Arzonetti, R. N. DeVoe–Holbein technology: New technology for closed-loop source reduction of toxic heavy metal wastes in the nuclear and metal finishing industries. In: *Proc. Massachusetts Hazardous Waste Source Reduction Conf.*, p. 66, 1984.
53. Lloyd, J. R., Harding, C. L., and Macaskie, L. E. Tc(VII) reduction and accumulation by immobilized cells of *Escherichia coli. Biotechnol. Bioeng.*, 55(3), 505–510, 1997.
54. Brock, T. D. and Gustafson, J. Ferric iron reduction by sulfur- and iron-oxidizing bacteria. *Appl. Environ. Microbiol.*, 32, 567–571, 1976.
55. Lloyd, J. R. and Macaskie, L. E. Bacterial reduction and removal of Technetium from solution. In: Doyle, F. M., Arbiter, N., and Kuyucak, N., Eds., *Mineral Processing and Extractive Metallurgy Review*, pp. 265–275. Gordon and Breach Science Publishers, Newark, NJ, 1998.
56. Park, D., Yun, Y. S., Jo, J. H., and Park, J. M. Effects of ionic strength, background electrolytes, heavy metals, and redox-active species on the reduction of hexavalent chromium by *Ecklonia* biomass. *J. Microbiol. Biotechnol.*, 15(4), 780–786, 2005.
57. Eary, L. E. and Schramke, J. A. Rates of inorganic oxidation reactions involving dissolved-oxygen. *ACS Symp. Ser.*, 416, 379–396, 1990.
58. Park, D., Yun, Y. S., Ahn, C. K., and Park, J. M. Kinetics of the reduction of hexavalent chromium with the brown seaweed *Ecklonia* biomass. *Chemosphere*, 66(5), 939–946, 2007.
59. Kusaka, E., Kamata, Y., Fukunaka, Y., and Nakahiro, Y. Effect of hydrolysed metal cations on the liquid–liquid extraction of silica fines with cetyltrimethylammonium chloride. *Colloids Surf. A*, 139, 155–162, 1998.
60. Godfrey, J. C. and Slater, M. J. *Liquid–Liquid Extraction Equipment*, p. 769. Wiley, 1994.
61. Jiang, H. and Guo, Q. X. Comparison of liquid–liquid extraction system and extraction–evaporation system for high concentrations of phenolic wastewater. *J. Environ. Eng.*, 133(2), 198–202, 2007.
62. Hammer, D. A. and Bastion, R. K. *Constructed Wetlands for Wastewater Treatment: Municipal, Industrial and Agricultural*, p. 831. Lewis Publishers, Chelsea, MI, 1989.
63. Feierabend, J. S. Wetlands: The lifeblood of wildlife. In: Hammer, D. A., Ed., *Constructed Wetlands for Wastewater Treatment: Municipal, Industrial and Agricultural*, pp. 107–118. Lewis Publishers, Chelsea, MI, 1989.
64. Emerick, J. C. and Cooper, D. J. Acid mine drainage in the west: The wetland approach. In: *Proc. 90th National Western Mining Conf.*, 1987. **Q5**
65. Wieder, R. K. Metal bonding to *Sphagnum* peat and sawdust: Relation to wetland treatment of metal polluted waters. *Water Air Soil Poll.*, 53, 391–400, 1990.
66. Reed, S. C. and Brown, D. S. Constructed wetland design—the first generation. *Water Environ. Res.*, 64, 776–781, 1992.
67. Henrot, J. and Wieder, R. K. Processes of iron and manganese retention in laboratory peat mesocosms subjected to acid mine drainage. *J. Environ. Quality*, 19, 312–320, 1990.
68. Haynes, R. J. and Goh, K. M. Ammonium and nitrate nutrition of plants. *Biol. Rev.*, 53, 495–505, 1978.
69. Hedin, R. S., Hyman, D. M., and Hammack, R. W. Implications of sulfate-reduction and pyrite formation processes for water quality in a constructed wetland: Preliminary observations. In: *Mine Drainage and Surface Land Reclamation, Mine Water and Mine Waste*. United States Department of the Interior, 1988. **Q6**
70. Gersberg, R. M., Elkins, B. V., Lyon, S. R., and Goldman, C. R. Role of aquatic plants in wastewater treatment by artificial wetlands. *Water Res.*, 20, 363–368, 1986.
71. Brodie, G. A., Hammer, D. A., and Tomljanovich, D. A. An evaluation of substrate types in constructed wetlands acid drainage treatment systems. In: *Mine Drainage and Surface Land Reclamation, Mine Water and Mine Waste*. United States Department of the Interior, 1988.
72. Michaud, R. and Richardson, P. K. Evaluation of the oxygen translocating capabilities of wetland plant species. In: Hammer, D. A. (Ed.), *Constructed Wetlands for Wastewater Treatment: Municipal, Industrial and Agricultural*, p. 831. Lewis Publishers, Chelsea, MI, 1989.
73. Meiorin, E. C. Urban runoff treatment in a fresh/brakish water marsh in Fremont, California. In: Hammer, D. A., Ed., *Constructed Wetlands for Wastewater Treatment: Municipal, Industrial and Agricultural*, p. 831. Lewis Publishers, Chelsea, MI, 1989.

74. Stark, L. R., Kolbash, R. L., Webster, H. J., Stevens, S. E. J., Dionis, K. A., and Murphy, E. R. The Simco #4 wetland: Biological patterns and performance of a wetland receiving mine drainage. In: *Mine Drainage and Surface Land Reclamation, Mine Water and Mine Waste*. United States Department of the Interior, 1988.
75. Wieder, R. K. and Lang, G. E. Fe, Al, Mn, and S chemistry of *Sphagnum* peat in four peatlands with different metal and sulfur input. *Water Air Soil Poll.*, 29, 309–320, 1986.
76. Spratt, A. K. and Wieder, R. K. Growth responses and iron uptake in *Sphagnum* plants and their relation to acid mine drainage treatment. In: *Mine Drainage and Surface Land Reclamation, Mine Water and Mine Waste*. United States Department of the Interior, 1988.
77. Gregory, E. and Staley, J. T. Widespread distribution of ability to oxidise Mn among freshwater bacteria. *Appl. Environ. Microbiol.*, 44, 2–13, 1982.
78. Jennett, J. C., Hassett, J. M., and Smith, J. E. Control of heavy metals in the environment using algae. International conference on the management and control of heavy metals in the environment, London, 1979.
79. Silver, M. Urban runoff treatment in a fresh brakish water marsh in Fremont, California. In: Hammer, D. A., Ed., *Constructed Wetlands for Wastewater Treatment: Municipal, Industrial and Agricultural*, p. 831. Lewis Publishers, Chelsea, MI, 1989.
80. Wildeman, T. R. and Laudon, L. S. Use of wetlands for treatment of environmental problems in mining: Non-coal-mining applications. In: Hammer, D. A. (Ed.), *Constructed Wetlands for Wastewater Treatment: Municipal, Industrial and Agricultural*, p. 831. Lewis Publishers, Chelsea, MI, 1989.
81. Hsu, P. H. Aluminum oxides and oxyhydroxides. In: Dixon, B. and Weed, S. B., Eds., *Minerals in Soil Environments*. Soil Science Society of America, Madison, WI, 1977.
82. Giblin, A. E., Bourg, A., Valiela, I., and Teal, J. M. Uptake and losses of heavy metals in sewage sludge by a New England salt marsh. *Amer. J. Bot.*, 67, 1059–1068, 1980.
Q7 83. Salim, R. Adsorption of lead on the suspended particles of river water. *Water Res.*, 423–429, 1983.
84. Hiel, M. T., Kerins, F. J. J., and Hammack, R. W. Tracy wetlands: A case study of two passive mine drainage treatment systems in Montana. In: *Mine Drainage and Surface Land Reclamation, Mine Water and Mine Waste*. United States Department of the Interior, 1988.
85. Kepler, D. A. An overview of the role of algae in the treatment of acid mine drainage. In: *Mine Drainage and Surface Land Reclamation, Mine Water and Mine Waste*. United States Department of the Interior, 1988.
86. Volesky, B., Ed. Biosorption and biosorbents. In: *Biosorption of Heavy Metals*, pp. 3–6. CRC Press, Boca Raton, FL, 1990.
87. Naja, G., Mustin, C., Berthelin, J., and Volesky, B. Lead biosorption study with *Rhizopus arrhizus* using a metal-based titration technique. *J. Colloid Interface Sci.*, 292(2), 537–543, 2005.
88. Naja, G., Deneux-Mustin, S., Mustin, C., Rouiller, J., Munier-Lamy, C., and Berthelin, J. Potentiometric titration: A dynamic method to study the metal binding mechanism of microbial biomass. In: Amils, R. and Ballester, A., Eds., *Biohydrometallurgy and the Environment Toward the Mining of the 21st Century (Part B). International Biohydrometallurgy Symposium—Proceedings*, pp. 201–210. Elsevier, Amsterdam, 1999.
89. Naja, G., Mustin, C., Volesky, B., and Berthelin, J. A high resolution titrator: A new approach to studying binding sites of microbial biosorbents. *Water Res.*, 39(4), 579–586, 2005.
90. Fourest, E. and Roux, J. C. Heavy metal biosorption by fungal mycelial by-products: Mechanism and influence of pH. *Appl. Microbiol. Biotechnol.*, 37, 399–403, 1992.
91. Friis, N. and Myers-Keith, P. Biosorption of uranium and lead by *Streptomyces longwoodensis*. *Biotechnol. Bioeng.*, 28, 21–28, 1986.
92. Niu, H., Xu, X. S., Wang, J. H., and Volesky, B. Removal of lead from aqueous solutions by *Penicillium* biomass. *Biotechnol. Bioeng.*, 42, 785–787, 1993.
93. Volesky, B. and Kuyucak, N. Biosorbent for gold. US Patent no. 4 769 233, 1988.
94. Volesky, B. and Tsezos, M. Separation of uranium by biosorption. US Patent no. 4 320 093, 1981.
95. Stamberg, K., Katzer, J., Prochazka, H., Jilek, R., Nemec, P., and Hulak, P. Canadian Patent no. 1 009 600, 1977.
96. Volesky, B. and Prasetyo, I. Cadmium removal in a biosorption column. *Biotechnol. Bioeng.*, 43, 1010–1015, 1994.
97. Kuyucak, N. and Volesky, B. The elution of gold sequestered on a natural biosorbent. *Biorecovery*, 1, 205–218, 1989.
98. Brierley, J. A., Brierley, C. L., Decker, R. F., and Goyak, G. M. Metal recovery. US Patent no. 4 789 481, 1988.

99. Dawkos, K., Lawry, P. V., and Walker, J. Evaluation of a constructed wetland to treat parking lot runoff. In: Hammer, D. A., Ed., *Constructed Wetlands for Wastewater Treatment: Municipal, Industrial and Agricultural*, p. 831. Lewis Publishers, Chelsea, MI, 1989.
100. Pelletier, T. End of the pipe? *Industry Week*, 38–57, 1991.
101. Holan, Z. R., Volesky, B., and Prasetyo, I. Biosorption of cadmium by biomass of marine algae. *Biotechnol. Bioeng.*, 41(8), 819–825, 1993.
102. Matheickal, J. T. and Yu, Q. Biosorption of lead from aqueous solutions by marine alga *Ecklonia radiata. Water Sci. Technol.*, 34(9), 1–7, 1996.
103. Jeffers, T. H., Ferguson, C. R., and Bennet, P. Biosorption of metal contaminants from acidic mine water. In: Smith, R. W. and Misra, M. (Eds), *Mineral Bioprocessing*, pp. 289–299. The Minerals, Metals, and Materials Society, 1991.
104. Mijango, F. and Diaz, M. Kinetics of copper ion exchange onto imminodiacetic resin. *Can. J. Chem. Eng.*, 72(12), 1028–1035, 1994.

BIBLIOGRAPHY

Cushnie, G. C. and Goldfarb, A. S. *Removal of Metals from Wastewater: Neutralization and Precipitation*, p. 232. Noyes Data Corporation/Noyes Publications, 1984.

Wachinski, A. M. and Etzel, J. E. *Environmental Ion Exchange: Principles and Design*, p. 131. CRC Press, Boca Raton, FL, 1996.

Kunin, R. *Ion Exchange Resins*, p. 466. Wiley, New York, 1959.

Parekh, B. S. *Reverse Osmosis Technology: Applications for High-Purity-Water Production*, p. 516. Marcel Dekker, Monticello, NY, 1988.

American Water Works Association. *Reverse Osmosis and Nanofiltration*, p. 173. American Water Works Association, Elbert, Colorado, 1998.

Lonsdale, H. K. *Reverse Osmosis Membrane Research*, p. 502. Plenum Publishing Corporation, 1972.

Jergensen, G. *Copper Leaching, Solvent Extraction and Electrowinning Technology*, p. 304. Society for Mining Metallurgy & Exploration, 1999.

Anderson, M. A. and Rubin, A. J. *Adsorption of Inorganics at Solid–Liquid Interfaces*, p. 357. Ann Arbor Science, Ann Arbor, MI, 1981.

Perrich, J. R. *Activated Carbon Adsorption for Wastewater Treatment*, p. 252. CRC Press, Boca Raton, FL, 1981.

Wallace, S. D. and Knight, R. L. *Small Scale Constructed Wetland Treatment Systems: Feasibility, Design Criteria and O&m Requirements*. Water Environment Research Foundation, 304 pp., 2006.

Okurut, T. O. *Pilot Study on Municipal Wastewater Treatment Using a Constructed Wetland in Uganda*. Taylor & Francis, 2000.

Odom, H. T. *Heavy Metals in the Environment: Using Wetlands for Their Removal*, p. 344. Lewis Publishers, Chelsea, MI, 2000.