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# Coagulant Recovery from Water Treatment Residuals: A Review of Applicable Technologies

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*Conventional water treatment consumes large quantities of coagulant and produces even greater volumes of sludge. Coagulant recovery (CR) presents an opportunity to reduce both the sludge quantities and the costs they incur, by regenerating and purifying coagulant before reuse. Recovery and purification must satisfy stringent potable regulations for harmful contaminants, while remaining competitive with commercial coagulants. These challenges have restricted uptake and lead research towards lower-gain, lower-risk alternatives. This review documents the context in which CR must be considered, before comparing the relative efficacies and bottlenecks of potential technologies, expediting identification of the major knowledge gaps and future research requirements.*

**KEY WORDS:** coagulant recovery, Donnan membrane, ultrafiltration, water treatment residuals, waterworks sludge

## 1. INTRODUCTION

Chemical-based treatment processes such as coagulant dosing have become well established because they are effective, easily controlled, and well understood. Historically, these practical benefits have had few drawbacks because: (1) Commercial ferric-, ferrous-, and aluminum-based coagulants have remained relatively inexpensive, with the unit cost of coagulant dosing in

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**TABLE 1.** A qualitative assessment of coagulant recovery against the principles of green chemistry

| Principles of green chemistry (Anastas and Warner, 1998)   | Comment on the potential impact of implementing in coagulant recovery   |
|--|---|
| 1. Prevent waste   | Significant reductions in the volume and metal content of sludge requiring treatment and disposal   |
| 2. Atom economy (maximizing the amount of dosed chemicals that are incorporated into the end product. Achieving this reduces waste volume and chemical demand) | This may allow more effective but expensive coagulants to be dosed, if they can be recycled more efficiently  |
| 3. Less hazardous chemical synthesis   | Quantities of metals leached into the environment (from landfill) will be reduced but recovery is reliant on the use of the strong mineral acids for resolubilization.  |
| 4. Designing safer chemicals   |   |
| 5. Safer solvents and auxiliaries  |   |
| 6. Design for energy efficiency  | Recovered coagulant will require separation from contaminants, using energy but this may be offset by the energy required to manufacture and transport virgin coagulant |
| 7. Use of renewable feedstocks   | The main principle of recovery is to renew coagulant supply internally  |
| 8. Reduce derivatives  | —   |
| 9. Catalysis   | Recycling coagulants moves their role from being a stoichiometric reagent to a retainable catalyst  |
| 10. Design for degradation   | Aluminum toxicity remains debatable but reducing quantities released into the environment reduces any potential risks and the need for monitoring                       |
| 11. Real-time analysis for pollution prevention  | The unavoidable use of acid in coagulant recovery does carry notable risks that will require management   |
| 12. Inherently safer chemistry for accident prevention   |   |

the order of 0.005 £/m<sup>3</sup> of treated water (Keeley et al., 2012), two orders of magnitude less than desalination (Zhou and Tol, 2005). (2) Prior to modern environmental regulations, the vast quantities of water treatment residuals (WTRs) produced by coagulation could be returned to the point of raw water abstraction, avoiding disposal costs (Walsh, 2009). (3) If disposal is needed, WTRs are considered inert, and their disposal has only incurred moderate costs.

Whilst conventional coagulant treatment is likely to remain a low-cost and popular option for contaminant removal for the foreseeable future, the process has become exposed to increased transport costs and global commodity prices as well as stricter environmental regulations and water quality standards. These challenges are common to many traditional chemical processes and typify the drivers for more sustainable, *green chemistry* (Anastas and Warner, 1998). The green chemistry concept aims to reinvent existing chemical processes with the minimum environmental impact and is defined by the 12 principles of green chemistry (Table 1). Many of these principles are applicable to chemical processes used in water treatment. Previous advances in sustainability in the water industry have focused on minimizing

energy usage and reuse of wastewater (WW) sludge (Water UK Sustainability Network, 2008). The principles of green chemistry may introduce water utilities to a more structured approach to make similar progress in the chemical processes used in potable treatment, moving towards the ideal of chemical-free treatment (United Kingdom Water Industry Research [UKWIR], 1999).

Conventional coagulant treatment has considerable scope for improved sustainability through coagulant recovery (CR), which enables the same atoms of coagulant metals to be repeatedly recycled and reused. To do this, acid is used to redissolve spent coagulant metals in waterworks sludge. Separation processes are then used to remove undesirable contaminants from the metal solution, before reuse. CR has the potential to reduce the environmental impacts of water treatment and satisfy many of the principles of green chemistry (Table 1).

When CR is viewed in the context of these principles, it becomes apparent that although it has potential to improve sustainability, it also has its own flaws. Acid-driven regeneration and purification stages must be considered holistically to ensure the benefits of CR are not offset by the chemical and energy demands of the recovery process.

This review seeks to assess the strengths and weaknesses of the available CR technologies, in relation to each other and in the wider context of WTR reuse strategies and sustainability agendas. This assessment will focus on the economic and environmental effects of CR as well as its impact on water treatment quality.

### 1.1. Coagulation

Before CR technologies can be assessed, it is important to outline the purpose of conventional coagulant treatment and the problems that it faces. This will highlight not only the value of CR but also the criteria it must satisfy. The objective of coagulant-enhanced flocculation and settlement is to remove the majority of suspended and colloidal particles from surface-abstracted raw water. Its effectiveness is reflected by its wide-scale application, with over 70% of water treatment works dosing coagulants as part of their treatment process (Betancourt and Rose, 2004). Advancements in water treatment have ensured that increasingly stringent consents on pesticides, micropollutants and disinfection by-products (DBPs) are met. The success of such treatments remains reliant on coagulation first removing turbidity and natural organic matter (NOM).

While coagulation–flocculation plays a key role in water treatment in removing the bulk of impurities from raw water, the process requires a large quantity of chemical and produces an even greater volume of sludge. For example, the United Kingdom uses more than 325,000 tonnes of coagulant each year. Aluminum- and ferric-based salts make up the majority of this total, with 107,000 and 165,000 tonnes, respectively (Henderson et al., 2009). At current prices, this equates to an annual cost of more than £28m. The

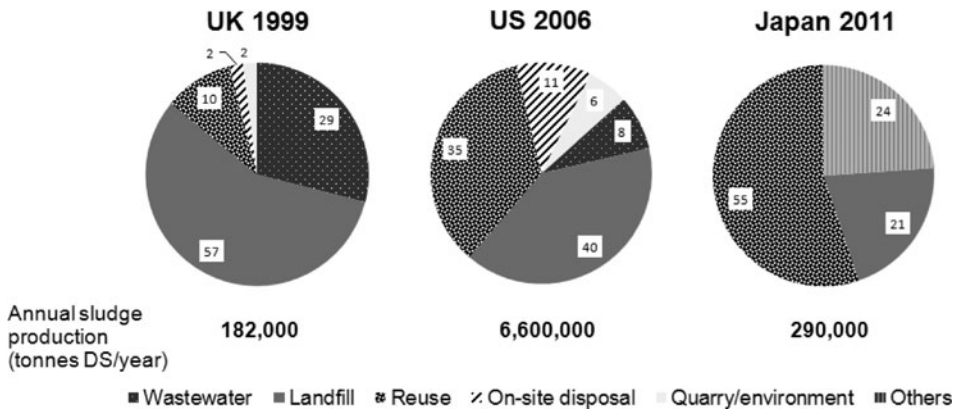
handling, transport, and eventual disposal of the resultant sludge pose further logistical and financial challenges.

Improved understanding of the scientific principles behind coagulation and process control has allowed dosages to be optimized. By ensuring only enough coagulant is dosed to achieve charge neutralization, rather than less efficient sweep flocculation, coagulant usage is minimized. Online monitoring and feedback control of coagulant dosing, using streaming current (Adgar et al., 2005) and ultraviolet absorbance at 254 nm (Wang and Hsieh, 2001), have allowed improved theoretical understanding to be put into practice. With the combination of other developments such as increased use of polymer as floc aids and pH optimization, coagulant dosing efficiency has been significantly improved. Changes in dosing practice can be illustrated by doses as high as 50 mg/L as Al in the 1970s (Westerhoff and Cornwell, 1978) compared to doses often below 10 mg/L as Al in current times (Jarvis et al., 2005). Dose optimization is only a partial solution to reducing coagulant demand, and is often compromised by demand for higher doses to ensure treatment robustness during periods of water quality deterioration (Hurst et al., 2004). Hence, once such optimization options have been fully exploited, recourse has to be made to CR as providing the only remaining option available for net coagulant demand minimization.

## 1.2. Sludge Disposal

The treatment and disposal of sludge is an equally important problem as coagulant usage in determining costs. In contrast to WW sludges, WTRs hold little nutritional or calorific value, making biological digestion or incineration impractical (Ulmert and Sarner, 2005). High concentrations of metals in the sludge limit the suitability for its disposal to land and the large quantities of bound water make dewatering and transport difficult and expensive (Babatunde and Zhao, 2007).

Prior to the introduction of prohibitive environmental regulations in Europe in 1946 (Babatunde and Zhao, 2007), it was common practice to return WTR to the same river that the raw water was abstracted (Elliott et al., 1990). In Europe, sludge is now mainly disposed to sewerage and landfill (Figure 1). Similarly in Japan, disposal of residuals to source was banned in 1971 by the Water Pollution Control Law (Miyano-shita et al., 2009). Japan appears to have utilized sludge reuse strategies more effectively than both the United States and United Kingdom (Figure 1), driven by an extreme scarcity of landfill capacity (Miyano-shita et al., 2009). From a survey of 46 North American utilities, it seems US regulations are not at the same stage, with 46% of WTRs disposed to source (Walsh, 2009). Changes in these regulations by the US Environment Protection Agency are expected but when and to what extent remains unknown (Cornwell, 2006).



**FIGURE 1.** A comparison of final sludge disposal locations in the United Kingdom, United States, and Japan as percentages of total sludge in surveys of water utilities. Adapted from Walsh (2009), UKWIR (1999), and Fujiwara (2011).

In 2000, more than 182,000 tonnes of sludge as dry solids were generated in the United Kingdom (Pan et al., 2004) with a disposal cost exceeding £5.5m (UKWIR, 1999). The equivalent figure for the United States exceeds 6.6 m tonnes per annum (Prakash and Sengupta, 2003). Sludge production is increasing, with some projecting it to have doubled between 2000 and 2010 (Albertin et al., 1990). This is due to population growth, regulatory changes, and increasingly variable raw water quality associated with climatic changes (Arnell, 1998; Hurst et al., 2004; Delpla et al., 2009). These increased sludge volumes, combined with rising transport costs and taxes designed to deter landfill expansion, place increasing pressure on water companies to minimize their waste production. A 10-fold increase in the United Kingdom inert landfill waste fees from £8 to £80 per tonne between 1996 and 2020 has been pledged by the UK government (Her Majesty's Treasury, 2010; Parsons and Daniels, 1999). This will force water utilities to adopt alternative disposal strategies or face the economic consequences.

Despite the cost, a significant proportion of waterworks sludge is still sent to landfill for disposal, with 57% in the United Kingdom and 40% in the United States (UKWIR, 1999; Walsh, 2009). Under the current European Union Council Directive 99/31/EC (1999), WTRs are considered an inert waste and are charged lower rate landfill gate fees accordingly. Some have suggested that the presence of regulated heavy metals may warrant reclassification and higher gate fees for WTRs (Elliott et al., 1990). However, landfill regulations are based on the metal content in leachate (EN 12457/1-4, 2002). Because the highly complexed WTR metals are not readily leached at moderate pH values, they are unlikely to present a problem in this respect (Elliott et al., 1990). However, metal toxicity is a contentious issue for reuse options that bring WTRs in contact with humans or their food chain (Babatunde

and Zhao, 2007). While this has held back WTR application to land, the concentrations of many metals (Cd, Cu, Cr, Pb, Zn, Ni) in WTRs are actually 10–35% lower than WW sludge (Elliott et al., 1990). Large amounts of WTRs are disposed to WW treatment plants and blended with WW sludge. Ultimately these WTRs are applied to land without exceeding metal leachability regulations (Figure 1), discounting concerns over WTR metal content.

As landfill and transport fees are generally charged on a mass basis, WTRs transported off-site for disposal are often thickened and dewatered to the minimal volume that is economical. Thickening achieves dry solids concentrations of 1–6% by adding polymer and using settlement. Further dewatering is made difficult and costly by chemically bound hydrated flocs (Babatunde and Zhao, 2007). Centrifuges, filter, and belt presses are used for this purpose (and at considerable expense) but dry solids above 20% are seldom reached. Less energy-intensive dewatering techniques such as lagoons, drying beds, and freeze-thaw have been considered (Walsh, 2009) but require large amounts of land (Fulton, 1973). Accordingly, on-site disposal is more common in the United States than in the United Kingdom, due to differing availability of land (Figure 1).

To avoid transport costs, gate fees and on-site treatment, unthickened WTRs are disposed to sewers whenever possible, with 25% of UK and 9% of US WTRs disposed this way. The US figure is lower, presumably because disposal to source is still permitted (UKWIR, 1999; Walsh, 2009). As utilities are often combined services, the treatment cost is not charged to the water treatment works but instead is imparted on the WW works. The true economic cost of this has been estimated using the Mogden formula to be approximately £35m per annum in the UK, almost 10 times more than the current amount actually spent on sludge disposal, according to available historical data (UKWIR, 1999). This true cost is partially offset by the benefits of incidental WW chemical treatment (see Section 5). A recent cost analysis determined that WTR disposal to the sewer was the most economical option, even when costs are charged to the potable works (Miyanoshita et al., 2009). However, the aims of improving sustainability go beyond simply finding the disposal route with the lowest economic cost. This is the sole appeal of disposal to sewer but other reuse options can offer further benefits to overall sustainability.

Because of the concerns raised by increasing coagulant cost, supply failure and the cost of sludge disposal, many reuse options have been considered. Success has been realized in the simple strategy of using WTRs as bulking agents in aggregates and soils (Babatunde and Zhao, 2007). Over a third of sludge in the United States is disposed in these ways (Figure 1). However, the actual benefit to the sludge recipient is often marginal. The true driver for reuse is the reduction in disposal costs for

the potable works. Attempts have also been made to reuse the remaining or regenerated chemical activity of the sludge, as an adsorbent or coagulant. Such roles offer greater rewards but require greater development and scientific precision to ensure public health is not compromised by contaminant carryover or accumulation as the coagulant is repeatedly recycled. Ambition of this kind is essential for the progression of sustainability within the water industry and will help resist increased treatment costs, carbon emissions, and waste production. Key to this is improving the scientific understanding of sludge and its constituents, allowing more efficient reuse of their unique characteristics without detriment from the associated impurities.

### 1.3. Sludge Characteristics and Content

Before the challenges and solutions of WTR reuse can be properly explained, an explanation of WTR characteristics is required. The nature of sludge is dependent on the source water quality and the chemicals dosed and account for a high level of WTR variability (Table 2). Mean and standard deviations for the main chemical components of sludge have been compiled from existing literature to give an indication of typical WTR properties and to their tendency to vary (Table 2).

Geotechnical analysis of thickened sludge from an upland source water dosed with alum highlighted the challenges of bulk reuse of untreated WTRs. The analysis described sludge as having high plasticity, high compressibility, and very low permeability (O'Kelly, 2008). These properties were attributed to the abundant coagulant-bound water, the high affinity of coagulant metal for water, the high organic content, and the charge destabilization within the flocs (O'Kelly, 2008). These characteristics make pure or untreated WTRs unsuitable for use as aggregates in engineering roles and help explain the difficulty in handling and transporting them. By treating WTRs or incorporating them with other materials, the impact of these characteristics can be reduced. Several trials have shown this approach to be successful and are discussed in more detail below.

Sludge bulk reuse options have recently been reviewed and are only included here to provide context for CR options (Babatunde and Zhao, 2007; United States Environmental Protection Agency [USEPA], 2011). Increasingly, the feasibility comparison is not between CR and landfill disposal but to other potential reuse options such as application to land, in aggregates and for WW treatment. As these options become more established, the marginal benefit of recycling coagulants is diminished, potentially making the return on the initial capital investment for CR harder to achieve during its operational lifetime.



**TABLE 2.** Compiled sludge loadings and variability

| Component        | Alum                                      |          | Ferric                    |                          | Wastewater, digested sludge <sup>a</sup> |                |
|------------------|---|----------|---------------------------|--------------------------|--|----------------|
|                  | Number of sludge samples                  | Units    | Mean (standard deviation) | Number of sludge samples |  | Units          |
| Total solids     | 20 <sup>b,c,d,g,h,i,k,l,n,o,p,r,s</sup>   | % w/w    | 5(6)                      | 7 <sup>a,h,m,p</sup>     | % w/w                                    | 4(6)           |
| Volatile solids  | 13 <sup>c,d,h,i,k,p</sup>                 | % of TS  | 29(18)                    | 5 <sup>a,m,p</sup>       | % of TS                                  | 18(9)          |
| Suspended solids | 5 <sup>h,k,p</sup>                        | % of TS  | 84(22)                    | 4 <sup>m,p</sup>         | % of TS                                  | 97(4)          |
| Al               | 29 <sup>c,d,f,g,h,i,k,l,n,o,p,r,s,t</sup> | % of TS  | 10(9)                     | 7 <sup>h,p,q</sup>       | % of TS                                  | 11(4)          |
| Fe               | 21 <sup>d,f,g,h,l,n,o,p,s,t</sup>         | % of TS  | 5(10)                     | 10 <sup>d,h,m,p,q</sup>  | % of TS                                  | 22(16)         |
| Mn               | 9 <sup>d,h,i,o,p,s</sup>                  | % of TS  | 0.71(1.54)                | 7 <sup>h,p,q</sup>       | % of TS                                  | 0.72(0.79)     |
| Pb               | 9 <sup>e,l,p,t</sup>                      | % of TS  | 0.038(0.069)              | 6 <sup>e,h,p,q</sup>     | % of TS                                  | 0.007(0.009)   |
| Ni               | 5 <sup>e,p,s</sup>                        | % of TS  | 0.005(0.002)              | 8 <sup>e,h,p,q</sup>     | % of TS                                  | 0.006(0.005)   |
| Cr               | 9 <sup>e,p,s,t</sup>                      | % of TS  | 0.003(0.003)              | 8 <sup>e,h,p,q</sup>     | % of TS                                  | 0.008(0.008)   |
| Cd               | 10 <sup>e,h,p,s,t</sup>                   | % of TS  | 0.006(0.016)              | 5 <sup>e,h,p</sup>       | % of TS                                  | 0.0002(0.0003) |
| Total Kjeldahl N | 4 <sup>h,s</sup>                          | mg/L (N) | 302(599)                  | 2 <sup>h</sup>           | mg/L (N)                                 | 793(858)       |
| Phosphate        | 8 <sup>f,h,p,s</sup>                      | mg/L (P) | 54(104)                   | 4 <sup>b,p</sup>         | mg/L (P)                                 | 23(24)         |
| BOD              | 4 <sup>h,h</sup>                          | mg/L     | 2595(2492)                | 2 <sup>h</sup>           | mg/L                                     | 211(168)       |
| pH               | 19 <sup>b,c,e,f,h,i,k,l,n,o,p,s</sup>     | —        | 6.5(1.4)                  | 8 <sup>g,m,p,q</sup>     | —  | 8.1(1.3)       |

Adapted from: a) Alonso-Alvarez et al. (2002); b) Bishop et al. (1987); c) Chen et al. (1976); d) Dymaczewski et al. (1997); e) Elliott et al. (1990); f) Gallimore et al. (1999); g) Georgantas and Grigoriopoulou (2005); h) Godbold et al. (2003); i) Jimenez et al. (2007); j) King et al. (1975); k) Lindsey and Tongkasame (1975); l) Petruzzelli et al. (2000); m) Pigeon et al. (1978); n) Prakash and Sengupta (2004); o) Sengupta (1994); p) Sotero-Santos et al. (2005); q) Tiishall and Hughes (2005); r) Ulmert and Sarner (2005); s) Wang et al. (1998); t) Xu et al. (2009a)

## 2. BULK REUSE OF WTRs

Bulk reuse of WTRs has seen them employed in two contrasting roles: as inert bulking material and as active substrates. The adsorbent properties and low cost of dewatered WTRs have prompted studies into their efficacy for contaminant removal from waste and ground waters. A long-term trial has shown the use of WTR sludge cake as a reed bed substrate to be effective at removing organic compounds and phosphorus (Zhao et al., 2009). Removals of 73% for chemical oxygen demand (COD), 83% for biological oxygen demand (BOD<sub>5</sub>), 86% for reactive P, 89% for soluble reactive P, and 78% for suspended solids (SS) were found. Forty-two percent of overall P removal was determined to be due to adsorption with the remainder by simple filtration. These results were considered promising but full-scale viability depends on a better understanding of bed clogging rates and lifetimes (Zhao et al., 2009). These issues should be kept in proportion however, as WTRs are in plentiful supply at only the cost of their transport and installation, making regular replacement a feasible option.

A related role is the use of WTRs permeable reactive barriers and the remediation of contaminated ground waters, at a lower cost than conventional zerovalent iron substrates. Using WTRs as a sorption substrate, uranium, cesium, chlorinated phenols, and nitro-benzenes have been successfully removed from contaminated ground waters at bench scale (Leskinen, 2011).

WTRs have been applied to soil and have been shown to improve soil structure by flocculating silica particles (Elliott and Dempsey, 1991). The low dewaterability of WTRs actually benefits this application, increasing soil moisture retention (Babatunde and Zhao, 2007). Concerns regarding the presence, availability, and toxicity of heavy metals from WTRs seem unfounded at this stage, while heavy metals are present in WTRs, research suggests that under neutral and alkali conditions, they are not readily bioavailable (Elliott et al., 1990). Examples of WTRs being used as inert bulking agents have been in bricks (Godbold et al., 2003) and cementous aggregates (Pan et al., 2004). When used to substitute 10% of conventional clay in bricks, no loss in structural integrity was observed (Godbold et al., 2003).

Bulk reuse strategies are limited by their failure to fully utilize the unique properties and constituents of WTRs. This makes them more a generic waste than a commodity and forces them to compete with numerous other waste producers seeking to obviate landfill disposal. There is a risk that the cost of additional transport and labor demanded by sludge reuse actually exceeds the economic benefit (Miyano-shita et al., 2009), but these costs are unlikely to be significantly more than conventional disposal to landfill. Legislation and perceived risk are also barriers to WTR bulk reuse (Babatunde and Zhao, 2007) but in comparison to the scrutiny that water treatment chemicals are subject to, these barriers can and have been negotiated (Figure 1).

### 3. CHEMICAL REUSE

Bulk reuse allows a step towards improved WTW sustainability, by reducing the amount of WTRs disposed, but it is incapable of reducing coagulant usage. In comparison, total reuse of the chemical value of WTRs could provide reductions in coagulant and disposal costs, and significant improvements to WTW sustainability. For these reasons, research into coagulant recycling technologies has a long history. The first patent in the area was granted in 1903, for the acidification of filter backwash water to resolubilize the precipitated hydroxides of metal coagulants (Jewell, 1903). Both Aluminum and iron have a linear solubility with acid dose: more coagulant is regenerated and returned to the aqueous phase as the pH is lowered. However, other sludge components such as NOM are also solubilized in acid, both increasing the acid requirement and contaminating the recovered coagulant. Contaminant co-solubilization is a key to the economics and quality of recovering coagulant for reuse in modern water treatment (USEPA, 2011) and remains the most critical barrier to CR for potable reuse.

#### 3.1. Recovered Coagulant Quality

In the 1970s and 1980s, when water quality regulations were less focused on DBPs and metals, nonselective CR was capable of providing acceptable levels of coagulant quality (King et al., 1975; Bishop et al., 1987). At its peak, the practice was adopted at 15 plants in Japan (White, 1984), as well as six pilot and full-scale trials at sites in the United States and United Kingdom (Webster, 1966; Saunders and Roeder, 1991). Improved sludge dewaterability was the primary aim of sludge acidification in Japan but the reuse of solubilized coagulant also bore a significant economic benefit (Tomono, 1977). Despite this success and progress, CR adoption and operation has been abandoned due to the following factors: (1) the failure of process control to manage the variability of WTRs (Chen et al., 1976), and (2) the accumulation of acid-soluble impurities, particularly manganese (Tomono, 1977; White, 1984). Acidification remains a possible dewatering aid (Fujiwara, 2011) but the solubilized liquor is unusable unless subsequently purified. This makes the practice economically viable in only when disposal routes are extremely limited.

In recent years, the control of DBPs in drinking water (particularly trihalomethanes; THMs) has become a focal point of modern potable quality. DBPs are formed from oxidation of organic material by chlorine and other oxidizing disinfectants. The resulting halo-organic compounds are suspected carcinogens and research has shown that at sufficiently high exposure, these compounds can heighten the risk of several cancers, particularly of the bladder (World Health Organization, 2000). DBP formation can be minimized by

limiting the availability of their reactants; the chlorine dose and the DBP organic precursors. While chlorine doses are already trimmed to prevent taste and odor complaints, the need for effective disinfection far outweighs any other treatment goals. The WHO has stated that the risk from pathogens, due to ineffective disinfection, is far greater than the risks caused by carcinogenic activity of DBPs, at the levels typically seen in treated water (World Health Organization, 2000).

Therefore, the emphasis for DBP management is on organic precursor removal, prior to disinfection. This is particularly important for the most reactive hydrophobic fractions with the highest THM formation potential. The risk of innovative treatment processes, such as CR, is the unknown impact they will have on DOC levels in treated water. CR, as any recycling process would, poses a particular risk of recycling DOC alongside recovered coagulant. This could lead to accumulation of DOC and elevation of the DBP formation potential of the treated water.

With the continued discovery and toxicological understanding of emerging DBPs, regulations are likely to become more comprehensive and stringent in the coming decades, putting further pressures on CR selectivity. With this regulatory background and future, utilities cannot afford to use unproven processes that pose any risk to treatment quality. Even in simple economic terms, any efficiency gains could quickly be outweighed by fines for breaching DBP regulations.

Public health is protected by regulation of these harmful compounds. National regulatory bodies have put limits on total THM levels at 100  $\mu\text{g/L}$  in the United Kingdom (Drinking Water Inspectorate [DWI], 2010) and 80  $\mu\text{g/L}$  in the United States (USEPA, 2011). US regulations also place a limit of 60  $\mu\text{g/L}$  on the total concentration of five haloacetic acids, another group of DBPs. It is likely that as more emerging DBPs are characterized and their toxicity is better understood, there will be more prescriptive regulatory guidelines.

CR causes varying amounts of organic compounds to be carried over with the coagulant dosed into the treatment stream, depending on recovery process performance (Table 3). Since only organic compounds that can be removed by coagulation will be present in WTRs and be present in the recycled coagulant, it could be surmised that the impact on treated water may be minimal since organic contaminants would be removed by the coagulant (Lindsey and Tongkasame, 1975). However, no research has been carried out on the effect that pH and interactions have on the transformation of NOM character during recovery. Contaminant loadings would have to be compensated by higher overall coagulant doses. Despite this, the reduced cost of recovered coagulant can allow higher doses, while still reducing chemical costs, in comparison to solely dosing fresh coagulant (Table 4).

Despite this, some studies have suggested that recycled coagulant does have a detrimental impact on treated water quality with respect to color

**TABLE 3.** Recovered coagulant quality at typical coagulant doses vs. current water quality standards for the US and UK

| Contaminant | Units           | US Maximum contaminant level (USEPA, 2009) | UK standard (DWI, 2010) | Commercial alum worst-case potential in treated water when dosed at 3.9 mg/L Al (Eyring et al., 2002) | Unselectively recovered alum worst-case potential conc. in treated water when dosed at 26 mg/L Al (Bishop et al., 1987) | Selectively recovered alum diluted when dosed at 3.9 mg/L recovered Al (Prakash and Sengupta, 2004) |
|-------------|-----------------|--|-------------------------|---|---|---|
| Aluminum    | $\mu\text{g/L}$ | (50–200)                                   | 200                     | 3900*   | 26000*  | 3900*   |
| Iron        | $\mu\text{g/L}$ | (300)                                      | 200                     | 7   | 3800  | 80  |
| Color       | Color units     | (15)                                       | 20                      | —   | —   | —   |
| Turbidity   | NTU             | 0.3–1–5                                    | 1 <sup>†</sup>          | —   | —   | —   |
| THM         | $\mu\text{g/L}$ | 80   | 100                     | — <sup>‡</sup>  | 214 (as THMFP)  | 14 (as DOC) <sup>§</sup>  |
| Manganese   | $\mu\text{g/L}$ | (50)                                       | 50                      | 0.2   | 3300  | —   |
| Nickel      | $\mu\text{g/L}$ | —  | 20                      | 0.7   | 0.8   | —   |
| Mercury     | $\mu\text{g/L}$ | 2  | 1                       | —   | 0   | —   |
| Copper      | $\mu\text{g/L}$ | 1300 (1000)                                | 2000                    | 1.0   | 7.8   | 0.9   |
| Chromium    | $\mu\text{g/L}$ | 100  | 50                      | 0.2   | 7.8   | —   |
| Lead        | $\mu\text{g/L}$ | 15   | 10                      | 0.2   | 0.5   | —   |
| Cadmium     | $\mu\text{g/L}$ | 5  | 5                       | 0.04  | 0   | —   |

\*Will largely be removed by precipitating as an insoluble hydroxide, meeting consented levels. Other components will also, to varying extents. <sup>†</sup>Upon entering the distribution network. <sup>‡</sup> Required by NSF Standard 60 to contribute less than 10% of final treated levels; here <8  $\mu\text{g/L}$ . <sup>§</sup> Used as a proxy in the absence of THM data.

**TABLE 4.** Dosing mass balance with and without coagulant recovery

| Alum dosed (mg/L)        | Coagulant dosing and recovery approach (DOC contaminant load mg/L in parentheses) |            |  |
|--------------------------|---|------------|--|
|                          | Conventional  | Recovered  | Recovered with 20% extra dose of fresh alum* |
| Recovered (81% of total) | 0   | 3.2 (11.5) | 3.2 (11.5)                                   |
| Fresh                    | 3.9   | 0.7        | 1.5  |
| Total                    | 3.9   | 3.9 (11.5) | 4.7 (11.5)                                   |

\*A hypothetical extra dose of coagulant to compensate for removal of organic contaminants carried over in recovered coagulant. Doses and recovery yield adapted from Eyring et al. (2002); and Prakash and Sengupta (2004).

(Lindsey and Tongkasame, 1975), although reported increases in trihalomethane formation potential (TTHMFP) have been small (Bishop et al., 1987). It is possible that current consents, of 80 and 100  $\mu\text{g/L}$  total THMs (in the United States and United Kingdom, respectively), would be breached if the organic matter retained in the recovered coagulant is not removed prior to chlorination. Indeed, the increasingly stringent water quality regulations have put pressure on commercial coagulant producers to reduce metal and organic contaminant levels in their products, which may be contributing to the increases in prices.

The quality standards that CR must adhere to, for potable use, go beyond THMs. For a recycled coagulant to be considered for dosing, it must meet the same quality assurance regulations as for virgin coagulants, as set out by Article 10 of the Council of the European Union Drinking Water Directive (1998). This implies that acid extraction alone is insufficient, as it could result in elevated DBP levels and impact public health. In the United Kingdom, coagulant quality regulation is implemented by British Standards for each coagulant type and the Drinking Water Inspectorate's (DWI) Regulation 31(4). In contrast, the United States uses a more general National Sanitation Foundation and American National Standards Institute, *Standard 60*, which considers coagulant purity in terms of their percentage contribution to treated water quality contaminant loadings (Table 3). Such standards are specifically aimed at commercial coagulants and make no mention of recovered coagulants and the issues surrounding their use, such as DOC concentrations. However, the recurrent message of water treatment chemical and treated water regulations is clear: treated water quality is of paramount importance and should be protected as much as is reasonably practicable. If they are to be implemented, CR technologies must satisfy this requirement and at least match conventional coagulant performance.

### 3.2. Solubilization

The process of metal solubilization is an unavoidable stage of CR but is unselective, with other contaminants solubilized as well. Recent CR research has

focused on developing efficient methods of metal-contaminant separation to prevent contamination of treated water by dosing recovered coagulant.

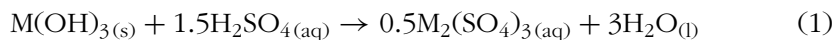
The end products of coagulant reactions with raw water are flocs of precipitated metal hydroxides, entrapped organic and inorganic contaminants, as well as insoluble metal-DOC (dissolved organic carbon) complexes. All CR technologies require the coagulant metals to be firstly returned to the aqueous phase. This stage accounts for at least 25% of the total operating costs for selective CR (Keeley et al., 2012). The most common method has been acidification using sulfuric acid, due to it being the cheapest acid available (Parsons and Daniels, 1999). Acidification is also responsible for reducing sludge volumes, as large amounts of suspended solids are dissolved (Saunders and Roeder, 1991).

For aluminum hydroxide, which is amphoteric, solubilization can also be achieved by raising the pH to form soluble aluminate salts  $[\text{Al}(\text{OH})_4]^-$ . At pH values above 11.4, Al recoveries of 80% have been achieved (Masschelein et al., 1985), at concentrations of 950 mg/L Al (Saunders and Roeder, 1991). However, the cost of sodium hydroxide is almost double that of sulfuric acid, per mol of acid or hydroxide (Alibaba, 2012; Keeley et al., 2012), making the process uncompetitive. Calcium hydroxide is a lower-cost alternative (Keeley et al., 2012) but offers only 50% Al recovery at pH values of 11.4 (Masschelein et al., 1985) and recovered concentrations of no more than 30 mg/L Al (Wang and Yang, 1975) due to the lower solubility of calcium over sodium aluminates. It has been reported that alkaline solubilization reduces the carryover of heavy metals, which are acid soluble (Masschelein et al., 1985), but coagulant quality is nonetheless impaired by increased solubilization of organic compounds (Isaac and Vahidi, 1961).

While acidification with sulfuric acid is the universal means of coagulant resolubilization, there is a lack of consensus on the optimum operational pH. More metal coagulant can be solubilized at lower pH values but this effect has been reported to diminish below pH values of 1, at concentrations of approximately 2,500 mg/L Al (Saunders and Roeder, 1991). Lower pH values require exponentially greater volumes of acid and drive up the process cost, as well as increasing organic solubilization. Optimum values between pH 2 and 4 have been reported to offer a compromise between metal and contaminant solubilization (Westerhoff and Cornwell, 1978; Bishop et al., 1987; Saunders and Roeder, 1991; Sengupta and Sengupta, 1993; Vaezi and Batebi, 2001). This is contrary to the theoretical pH-solubility curves for aluminum that suggest a linear increase in solubilization to a maximum at pH 2.75. This has been attributed to mass transfer limitations, such that once aluminum hydroxide salts are solubilized only the less reactive oxide forms remain (Saunders and Roeder, 1991).

Acid solubilization has also been considered in terms of the stoichiometric ratio between the trivalent coagulant metal hydroxides and the added sulfuric acid. Stoichiometry would suggest 1.5 mol of acid are required to

solubilize 1 mol of trivalent metal (M) (Eq. (1)).



Experimental data has shown higher molar ratios are usually required, with the actual molar ratio being closer to 2:1 (Bishop et al., 1987): additional acid is required to overcome the buffering capacity of the sludge, reflecting the original raw water characteristics. However, other studies have found the 1.5:1 stoichiometric amount to be sufficient for 100% coagulant solubilization (Ulmert and Sarner, 2005). Since the specific acid requirement for metal solubilization is a major cost factor, attempts have been made to actively reduce the dose required. Sodium sulfide has been used to reduce the oxidation state of ferric salts to ferrous, reducing the acid:metal molar ratio to 1:1. The settled volume of the remaining insoluble fraction was reduced to 20% of the original (Pigeon et al., 1978). However, removal of residual sulfide was required before the recovered coagulant could be reused, to prevent iron sulfide formation (Pigeon et al., 1978). The demand for costly sodium sulfide by this process also significantly compromises the cost benefit.

The extent of solubilization is not the only consideration for pH adjustment. If acid insoluble recovery residuals are disposed to landfill as inert waste, a minimum pH limit may be imposed to prevent metal leaching (Bishop et al., 1987). It may be more economical not to acidify the sludge below this limit to avoid neutralization later. Sludge settleability is also dependent on pH and, while acid extraction reduces the mass of suspended solids in the sludge, residual solids require removal and disposal. Studies have shown that optimum settling rates of the acid insoluble WTR fraction occurred at pH values of 2–3, providing another incentive for restraint in acidification (Sengupta and Sengupta, 1993).

Another way of improving the process economics is to consider reusing the acid used to recover coagulant. Suitable selective acid recovery technologies are discussed alongside CR below.

#### 4. CR SEPARATION TECHNOLOGIES

The success of recovering coagulant to a standard satisfying modern potable regulations depends on efficient metal-contaminant separation within the acidified sludge solution. Achieving this requirement allows the full benefits of CR to be realized and the satisfaction of many of the principles of green chemistry (Table 1). The earliest, simpler coagulant recycling technologies used solid–liquid filtration or settlement to remove only gross solids from the recovered coagulant (Jewell, 1903; Fulton, 1973). This is still practiced but modern systems also use molecular charge and size to discriminate metal



coagulants from contaminants. These principles have been applied using membranes and adsorbents.

The heterogeneous nature of potential contaminants in recovered coagulant poses a significant challenge. Natural organic compounds vary widely in molecular weight, functionality and depend heavily on environmental conditions, while heavy metals share similar cationic and molecular weight characteristics with coagulants. These characteristics make total exclusion from the recovery of trivalent metal coagulants difficult. Despite this, several separation processes have reported recovery of high purity coagulant, with minimal heavy metal and organic compound contaminants (Prakash and Sengupta, 2003; Ulmert and Sarner, 2005). These can be categorized as either pressure-driven membranes or charge-based methods.

#### 4.1. Pressure-Driven Membrane Separation

Pressure-driven membranes are widely used separation technologies in water treatment. The combined benefit of a near absolute barrier and simple and well-understood operation seemingly make them candidates for CR. However, issues such as fouling, energy demand, and limited selectivity have been cited as reasons to disregard conventional membrane treatment for CR (Prakash and Sengupta, 2003).

There have been a number of studies of the performance of ultrafiltration (UF) for CR at bench and pilot scale (Lindsey and Tongkasame, 1975; Ulmert and Sarner, 2005). In these studies, the rationale was to select UF pore sizes allowing trivalent metal permeation whilst retaining NOM. A range of membranes with differing molecular weight cutoffs (MWCO) between 10–50 kDa have been investigated to determine the greatest margin of metal-contaminant separation achievable. Membranes with MWCO of 10 kDa allowed aluminum permeation exceeding 90% and TOC rejections of 50–66% (Lindsey and Tongkasame, 1975).

Jar tests were used to compare the efficacy of recovered and fresh coagulant at various doses. At doses that gave the best level of treatment, the presence of organic contaminants in the recovered coagulant had no detrimental effect on treated water quality. At doses below the optimum, there was an increase in treated water residual color, which worsened with repeated recycles (Lindsey and Tongkasame, 1975). Subsequent runs showed sharp declines in fluxes, due to the concentrated feed solution forming a gel layer on the membrane surface. This was shown to be managed effectively with water washes every 12 hr and weekly washes with 0.01 M sodium hydroxide (Lindsey and Tongkasame, 1975). It should be noted that this study was carried out before DBPs were a water quality issue. Therefore the research did not focus on the impact the recovered alum had on DOC levels in the treated water.

Economic management of the inevitable fouling of pressure-filtration membranes is a key to successful treatment of a concentrated, acidified sludge feed. Contradictory arguments have been made regarding the positive (Lindsey and Tongkasame, 1975) and negative (Ulmert, 2005) cost-benefit of pressure-filtration for CR. This debate is likely to continue, but even based on pessimistic performance estimates, membrane filtration appears to offer the lowest cost of all options (Keeley et al., 2012).

A study of an aluminum recovery process, known as the *ReAl* process, used UF followed by diafiltration, nanofiltration (NF), and precipitation to purify and concentrate alum to a crystalline form (Ulmert and Sarner, 2005). Again, a range of UF membrane MWCOs between 2 and 100 kDa were considered. The membranes with a cutoff less than 5 kDa allowed only 55–65% Al recovery and COD rejections of 80%. Since even the most hydrated form of aluminum sulfate (heptadecahydrate) has a molecular weight well below 1 kDa (Smith, 1942), the retention of aluminum at larger MWCOs strongly suggests that aluminum is complexed with larger organic molecules. Further Al recovery may be achieved by degrading these organo-metallic complexes but also risks reducing DOC molecular weights and increasing DOC permeation.

For the *ReAl* process, optimum separation was achieved using a membrane with a MWCO range of 15–30 kDa, giving Al recovery of 94% and COD rejection of 78%. Without further purification, this was deemed to be of insufficient quality for potable treatment but was suitable for dosing into waste water for phosphorus removal. For further purification, the *ReAl* process concentrates the recovered coagulant using NF (by permeation of water), cooling the retentate to 0 °C and adding potassium sulfate to induce alum precipitation. The crystals were then filtered and washed with cold water to remove aqueous organic contaminants. Ultimately a sufficiently high level of purity was reached, with a heavy metal content was below European regulations for coagulants and TOC content was in the order of 100 mg/kg of Al (Ulmert and Sarner, 2005). Approximately 10% of Al permeated through the NF membrane but it was proposed that some use could still be made of it in WW treatment. The economics of such a thorough purification process were not described in the paper, though process costs would be expected to be high.

#### 4.2. Charge-Based Separation

While conventional membranes can be used for coagulant-contaminant separation, such processes face the challenge of overcoming fouling and quality issues. Due to the overlap in molecular weights of coagulants and organic contaminants, some of the most successful coagulant separation technologies have used molecular charge as the principal means of discriminating between cationic coagulant metals and anionic or neutral contaminants. These have

been in the form of ion-exchange media—as liquids, resins, and dialysis membranes.

#### 4.2.1. LIQUID ION EXCHANGE

The first charged-based separation technology used to remove organic contaminants from acidified sludge was liquid ion exchange (LIE; Cornwell, 1979). First, the impure acidified coagulant is mixed with an organically soluble extractant liquid, into which the coagulant metals are adsorbed, forming organic-metal complexes. When saturated with metal, the extractant is dissolved in an organic hydrophobic solvent (such as kerosene) and removed from the acidified sludge. The organic solution is then mixed with an acid stripping solution that recovers the coagulant and regenerates the extractant. The purified recovered alum is then ready for reuse or further purification, if required, and the stripped extractant can be recycled back to the first step. Because the extractant is specific for Al, the organic matter rejection, heavy metal rejection, and coagulant quality are high. Alum recoveries of >90% were achieved, at concentrations and quality equal to, or better than, commercial-grade equivalents of the time (Westerhoff and Cornwell, 1978). This favorable comparison may not be valid against modern commercial coagulants which have to treat water to satisfy DBP consents.

More detailed research for full-scale LIE plants supports the positive outcomes of bench-scale studies, with alum recoveries still in excess of 90% (Cornwell et al., 1981). Coagulant performance, in terms of THM precursor concentrations, color and turbidity removals, was comparable to commercial coagulants at the same dose. The conclusions of an economic assessment in the same report suggested that LIE recovery of alum would offer operating cost reductions over conventional coagulant use, provided Al concentration in WTRs exceeded 1,200 mg/L, and the WTR flow was at least 37 L min<sup>-1</sup>. Increasing these two parameters was shown to increase operating cost savings (Cornwell et al., 1981). Criticism aimed at the inability of LIE to concentrate recovered aluminum seems unfounded (Sengupta and Prakash, 2002). No concentration takes place during the extraction phase but four-fold concentration increases have been reported in the stripping phase, producing recovered alum concentrations above 30,000 mg/L as Al (Cornwell et al., 1981).

Concern has been expressed over the nature of the chemicals used in the LIE process (Sengupta and Sengupta, 1993). There is potential for entrainment of organic solvent in the coagulant during the stripping stage and contamination of the treated water (Prakash and Sengupta, 2003), although an activated carbon polishing stage was originally suggested to prevent this (Cornwell et al., 1981). Similar techniques are used in extractive hydrometallurgy, where these limitations are less important. In hydrometallurgy, end products do not have to be fit for human consumption, and process complexity is justified by the recovery of higher value metals (Tasker et al., 2007).

Although capable of impressive recovery rates and yields, LIE is vulnerable to entrainment of liquid organic extractants and solvents, elevating the risk of taste and odor complaints and DBP formation. Polishing stages can be used to help mitigate this risk but would worsen the already marginal cost-benefit of recovering low-value coagulants. Accordingly, research has focused on more robust solid-phase ion-exchange systems.

#### 4.2.2. ION-EXCHANGE RESINS

Attached and suspended ion-exchange media were a logical progression from LIE. Because the extractants (resins beads) are less toxic and more readily retained, the danger of treatment stream contamination is minimized, allowing a simpler and safe recovery process.

Adsorbent resins have been used in a number of ways to purify recovered coagulant. This includes selective adsorption of cationic coagulant metals from an acidified solution, leaving anionic contaminants in solution (Sengupta, 1994; Petruzzelli et al., 2000) or selective adsorption of anionic contaminants, leaving cationic coagulant metals in solution (Anderson and Kolarik, 1994). Once saturated, the resins can then be stripped and regenerated on-site. The relative concentration of metal coagulant to anionic contaminants governs which process is most suitable, making adsorption of anionic contaminants a possible polishing stage that could be used after other separation techniques.

Column-based weak carboxylate Purolite C106 and strong sulfonic Purolite C100×10 cation-exchange resins have both demonstrated >90% recovery of Al from acidified alum sludge, but the sulfonic resin required more sodium hydroxide for regeneration (Petruzzelli et al., 2000). Aluminum concentrations of 5,000 mg/L as Al were recovered in hydroxide form, but would require acidification and further chemical treatment to generate an acidic sulfate or chloride coagulant salt. A 50 L/d pilot-scale *ion-exchange recovery of aluminum process (IERAL)* employing Purolite C106 resins reportedly achieved Al recovery yields of 95%. Using hydroxide precipitation and acid resolubilization, aluminum sulfate concentrations of 99% were achieved, equaling commercial coagulant purity (Petruzzelli et al., 2000). When operated as an exchange column at a flow of 5 bed volumes (BV) per hour, breakthrough started at 80 BV and total Al breakthrough occurred at 150 BV, yielding a very low capacity and treatment rate. This protracted period of breakthrough is indicative of the declining rates of adsorption as the ion-exchange resins approach Al saturation and equilibrium—a limitation common to all ion-exchange processes (Prakash and Sengupta, 2003). Resin regeneration and metal stripping is carried out with sodium hydroxide, forming metal hydroxide precipitates that can be filtered before acid solubilization. While this extra stage allows higher coagulant concentrations than other processes, it requires an additional adjustment of pH, additional chemicals, and increased costs.

An alternative to column processes are conveyor belts with attached resins. These allow simultaneous loading and stripping of the resins, as they cycle between tanks of acidified sludge feed (with 90% of the Al in the original sludge extracted) and stripping acid (Sengupta and Sengupta, 1993). A bench-scale simulation of this process, using weak acid resin beads (iminodiacetyl) attached to a porous PTFE membrane, recovered 68% of Al with 12% DOC and almost total exclusion of heavy metals, independent of their feed concentrations. Although selective, this process provided low concentrations of recovered Al, at only 400 mg/L after 30 cumulative cycles. Further cycles increased the Al concentration but at the expense of decreased NOM exclusion (Sengupta and Sengupta, 1993). However, this system does have the advantage of using an acidic stripping agent, reducing the need for further pH manipulation, in contrast to the Purolite resins used in columns.

Although there are no examples of using ion-exchange resins for ferric CR, there are numerous examples of ferric extraction from similar acidified waste streams, for example, electroplating (Saji et al., 1998; Agrawal and Sahu, 2009; Navarro et al., 2009). The principles of these processes are transferrable to ferric CR but with certain constraints: co-extraction of other metal species and the use of toxic or easily entrained extractant or stripping agents are unacceptable. These constraints, combined with the requirement for acidification prior to separation (whereas electroplating streams are already acidified), greatly impair the economics of technology transfer.

Anion-exchange resins show potential at selectively adsorbing organic contaminants from otherwise pure acidified coagulant. Because selective recovery processes are still prone to some organic carryover, anion-exchange resins may prove valuable in ensuring the absence of THM precursors in recycled coagulant. Following previous purification by polyelectrolyte and pH-induced contaminant precipitation, TOC levels in recovered coagulant were reduced from 120 to 40 mg/L by passing through a column of Amberlite IRA 910 resin in the hydroxyl form (Anderson and Kolarik, 1994). In conjunction with more effective pretreatment, anionic resins could help reduce the recovered coagulant organic content to beneath regulated levels. However, the heterogeneity of NOM character should be remembered. The DOC fractions that have not been removed by other technologies are likely to be low-molecular weight hydrophilic compounds and will not be removed effectively by anionic resins either.

A more crude method demonstrated that charcoal dosed at 10,000 mg/L into a solution containing 6,000 mg/L as Al was capable of removing 34% of the color from the coagulant in 5 min of mixing (Abdo et al., 1993). Although the performance is comparable to anion-exchange membranes, recovery and regeneration of the charcoal would be more costly. In this example, further purification was achieved by evaporation and crystallization.

Ion-exchange resins and adsorbents allow improved retention over LIE and are capable of recovering relatively pure coagulant without undue process complexity. Like most ion-exchange processes, practical applicability is limited by slow diffusion kinetics for extraction and stripping. The cost of using a stoichiometric excess of sodium hydroxide to strip-bound coagulant metals and to regenerate the resin largely offsets the value of the recovered coagulant (Petruzzelli et al., 2000). At current alum and sodium hydroxide prices, the cost of using of 6 mol of hydroxide to recover 1 mol of aluminum approaches parity with commercial coagulant, limiting its appeal (Petruzzelli et al., 2000; Alibaba, 2012; Keeley et al., 2012). Such inefficient use of chemicals would also undermine any potential benefits brought about by CR, in terms of striving for a green chemical process. Until more efficient media and regeneration techniques are developed, ion exchange does not appear to be viable for CR.

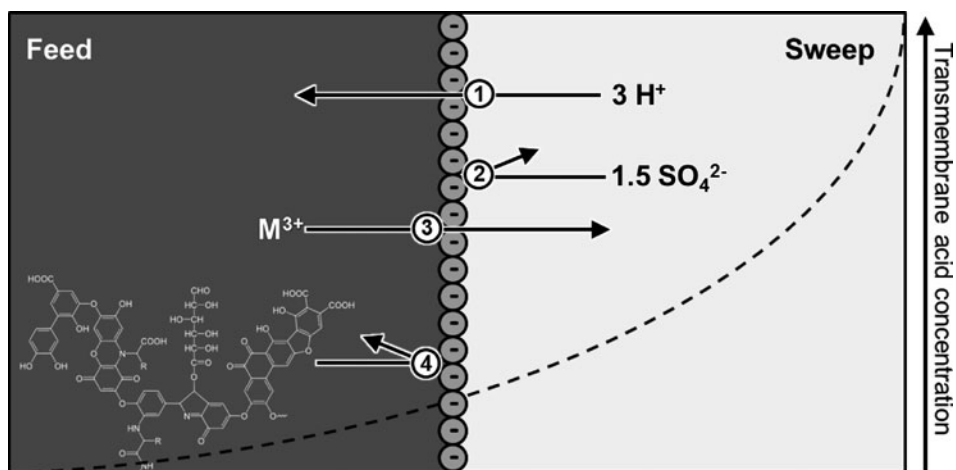
#### 4.2.3. DONNAN MEMBRANE PROCESSES

Resin-based recovery processes are simpler processes when compared to LIE but are still based on a two-step, extract/strip operation. Donnan dialysis membranes allow these two steps to occur simultaneously through an ionic membrane that separates the feed and stripping solutions. This configuration makes plug-flow operation easier to implement, ameliorating the kinetic limitations of resin-based batch processes.

Donnan membranes are ion-selective (for cations in the case of CR), and ion flux is driven by electrochemical gradients, as opposed to pressure differentials of conventional membrane processes. The lack of transmembrane pressure helps minimize fouling; the flux is determined only by the electrochemical gradient and the membrane characteristics (Prakash and Sengupta, 2003).

Metal recovery is driven by the Donnan co-ion exclusion principle (Donnan, 1924). The recovery solution, containing a more concentrated acid solution than the feed, creates an  $H^+$  concentration gradient across the membrane. The cation-selective membrane allows  $H^+$  ions to diffuse across it, to achieve thermodynamic equilibrium. The sulfate co-ions are rejected by the cation-selective membrane, creating an electrochemical gradient across the membrane (Figure 2). Another application of this principle, hydrogen fuel cells, employs this electrochemical gradient to produce electrical work. For CR it is used to drive coagulant metal ions from the feed to the recovery solutions (Prakash et al., 2004).

Because metal ion movement across the membrane is driven by electrochemical potential, metals can be transported against their concentration gradient, allowing concentrated solutions to be recovered. Organic contaminants are largely rejected by the cation-selective membranes along with di and monovalent heavy metals (Prakash and Sengupta, 2003), which remain in stable organic complexes (Elliott et al., 1990). Bench-scale performance

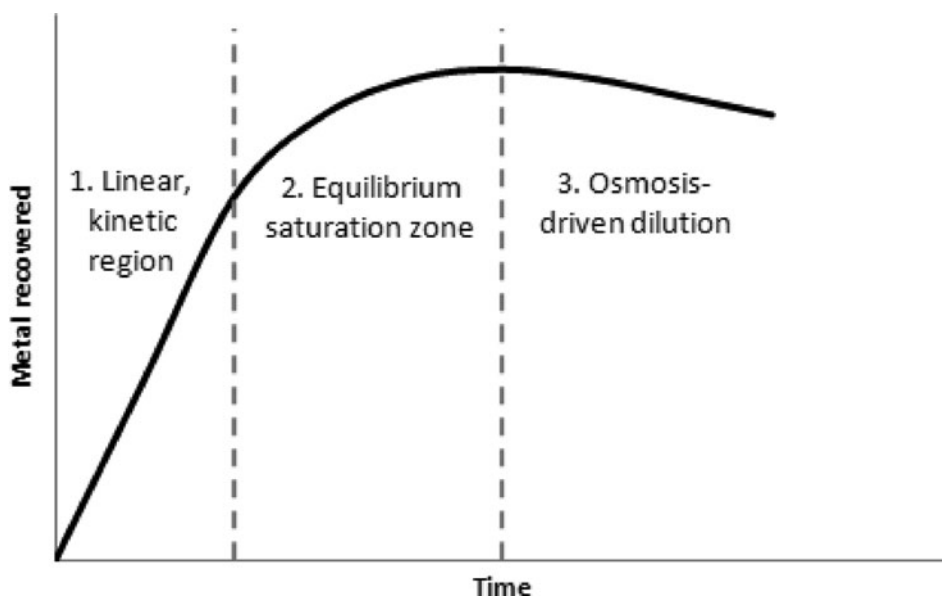


**FIGURE 2.** Donnan equilibria-driven trivalent metal recovery across a cation-selective membrane. 1. Sweep-side acid protons move down their concentration gradient across the cation-selective membrane, creating a charge imbalance across the membrane. 2. Acid counterions are rejected by the membrane, preventing them moving to correct the charge imbalance. 3. Trivalent metals move in the opposite direction to acid, neutralizing the transmembrane charge. 4. Organic material in the feed is rejected by the membrane due to its bulk and negative/neutral charge.

studies have shown recovered concentrations of 5,650 mg/L Al (72% recovery) with only 3.5 mg/L DOC, from a feed solution with initial concentrations of 2,500 mg/L Al and 190 mg/L DOC, with no noticeable membrane fouling. Incidental recovery of ferric ions was also reported, to a concentration of 97 mg/L, but this was deemed to benefit coagulant performance rather than impair it.

The selectivity of this process has been shown to be variable, however, with a subsequent trial recovering less aluminum (4,725 mg/L concentration and 81% yield) with more DOC carried over (17 mg/L), from a feed of 1,900 mg/L Al and 150–600 mg/L DOC, in the same period of dialysis (Prakash et al., 2004). The correlation between elevated feed DOC and increased DOC permeation would suggest feed quality has a significant impact on the quality of recovered coagulant. Recovery of ferric ions, from a sludge where ferric was used as a coagulant, gave almost identical performance to that of alum sludges, with recovered concentrations of 5,500 mg/L Fe from a feed of 1,800 mg/L (76% yield) (Prakash and Sengupta, 2003).

Yield percentages and concentrations are important but process kinetics are also key to full-scale success. In the case of Donnan diffusion, rates are dependent on many factors. These include feed and recovery-side concentrations, membrane thickness and ionic capacity, and recovered metal valency. Aluminum-acid interdiffusion rates in the kinetic region of exchange (Figure 3) approached those of protons (Prakash and Sengupta, 2003). This was attributed to the high affinity of trivalent metals for the strong-acid ionic



**FIGURE 3.** Kinetic regions that occur as batch Donnan dialysis progresses. Adapted from Prakash and Sengupta (2004).

groups on the Nafion 117 ion-exchange membrane, saturating all the available sites and ensuring that only the rapid interdiffusion of protons limit the reaction. However, the same data also showed that this accelerated rate is short-lived. After 6 hr and approximately 65% Al recovery (Prakash and Sengupta, 2003), the batch ion-exchange system approached equilibrium, slowing interdiffusion (Figure 3). If diffusion is allowed to continue beyond this point, background osmotic leakage overcomes the diminished ionic transfer rates and dilutes the recovered solution (Figure 3).

Published Donnan performance is impressive, and its resilience to fouling is an attraction in the CR role. However, when the diffusion time (24 hr) and specific membrane area ( $120 \text{ cm}^2/\text{L}$  of feed) are taken into consideration (Prakash and Sengupta, 2003), the cost benefit of the process is questionable (Keeley et al., 2012). Reasons such as these have limited the practical application of the Donnan process (Strathmann, 2010), particularly in the recovery of ions from concentrated wastes (Wang et al., 2010). Slow kinetics can be compensated for by using greater membrane area contact time but this requires greater quantities of expensive membranes. Diffusion rates will also decline as the process reaches equilibrium. This requires a balance to be struck between recovery yield (i.e., acid requirement) and specific membrane area requirements.

Membrane functionality is important, with superior diffusion rates for aluminum recovery (Table 5) demonstrated by homogeneous sulfonated membranes. These membranes have demonstrated rates 5 to 10 times greater than heterogeneous alternatives as well as being 30 times more selective for



**TABLE 5.** Normalized Donnan dialysis initial flux performance comparison for trivalent metal recovery with a 1 M sulfuric acid sweep solution

| Membrane type                             | Functionality or other variable               | $J_{\text{salt}}$ (eq/m <sup>2</sup> /s) over initial 4 hr with 1 M H <sub>2</sub> SO <sub>4</sub> sweep solution | Ion              | References                  |
|---|---|---|------------------|-----------------------------|
| DuPont Nafion 117                         | Homogeneous sulfonated PTFE                   | $8.27 \times 10^{-4}$   | Al <sup>3+</sup> | Prakash and Sengupta (2003) |
| DuPont Nafion 117                         | Homogeneous sulfonated PTFE                   | $2.13 \times 10^{-4}$   | Fe <sup>3+</sup> |                             |
| DuPont Nafion 117                         | Homogeneous sulfonated PTFE                   | $8.46 \times 10^{-4}$   | Al <sup>3+</sup> | Prakash et al. (2004)       |
| Sybron Chemicals Ionac MC 3470            | Heterogeneous sulfonated (reinforced) polymer | $7.34 \times 10^{-5}$   | Al <sup>3+</sup> |                             |
| Gelman Sciences ICE-450 SA <sub>3</sub> S | Homogeneous sulfonated polyester              | $2.25 \times 10^{-5}$   | Cr <sup>3+</sup> | Tor et al. (2004)           |
| Gelman Sciences ICE-450 SA <sub>3</sub> T | Heterogeneous sulfonated polyester            | $2.07 \times 10^{-5}$   | Cr <sup>3+</sup> |                             |

Al (Prakash and Sengupta, 2005). This was attributed to Nafion membranes being more hydrophilic and the even distribution of sulfonate ionogenic groups, throughout the membrane cross section, allowing more direct diffusion paths for ions (Prakash and Sengupta, 2005). This effect was less pronounced in a similar study investigating the relative performance of heterogeneous and homogeneous membranes for the Donnan transport of Cr<sup>3+</sup> ions (Table 5) due to the importance of other factors such as ion characteristics, membrane thickness, and hydrophilicity. The four-fold variation of diffusion rates for aluminum and ferric ions diffusing through the same membrane (Table 5) contradicts the theory that valency is the principle rate-determining characteristic for interdiffusion rates (Prakash and Sengupta, 2003). The practical outcome of this difference is a further increased specific membrane requirement for ferric CR over alum.

A study of divalent magnesium and calcium recovery from lime softening sludge, using Nafion 117 homogenous membrane, showed notably lower flux performance over the initial 4 hr, at just  $2.31 \times 10^{-5}$  eq/m<sup>2</sup>/s (Wang et al., 2010). This may be due to limiting mass transfer, caused by the feed solution being almost four times more dilute than other experiments using the same membrane (normalized in terms of eq/L; Prakash and Sengupta, 2003), or the higher stability of divalent organic complexes over trivalent (Elliott et al., 1990). These effects were sufficient to offset the hypothesized higher flux of the lower valence magnesium and calcium species, in comparison to aluminum and ferric, due to the bivalent species having less electrostatic

attraction to the counterions within the membrane, allowing for more labile transfer (Tor et al., 2004).

Because the direction of acid transport is in the opposite direction to recovered metal, Donnan dialysis will generate an acidified waste stream at the end of the recovery process. At the point that the recovery system reaches thermodynamic equilibrium, the aluminum depleted feed solution is highly acidified, requiring neutralization prior to disposal. Like all selective recovery processes, there are significant issues regarding the degree of contamination and coagulant concentration: both must be addressed for reuse. Although DOC transport is minimal with Donnan dialysis, even levels as low as this may be sufficient to fail coagulant quality regulations or THM consents.

Selective anion adsorbents may be a necessary augmentation to ensure that the product is acceptably pure. This would add another level of complexity to the process but, since only a small amount of NOM is required to be removed, the adsorbent would require less frequent regeneration compared to less-selective separation processes. Furthermore, while Donnan dialysis facilitates metal ion concentration, typically by a factor of three (Prakash and Sengupta, 2003), it still does not match the concentration of commercial coagulants of approximately 40,000 mg/L as Al for alum. This dilution may help ensure better distribution of coagulant, particularly with static mixers but would impair the ease of handling and transport and must be considered before full-scale implementation.

Donnan dialysis also shows potential to recover acid from the recovered coagulant stream and the wasted feed stream. Using an anion-selective (but proton permeable) membrane to separate the impure acid solution from a solution of deionized water creates a sulfate concentration gradient and anion movement across the membrane. To maintain electroneutrality across the membrane, protons diffuse through the membrane via a tunneling mechanism. This has been used to recover sulfuric acid, at yields of 85% and concentrations of 4 mol/L as  $H^+$ , from a feed of 4.78 mol/L  $H^+$  (Xu et al., 2009b). In this example, leakage of the contaminant ion, ( $Al^{3+}$ ), was less than 5%. If applied to acid recovery from WTRs, contaminant leakage may be significantly higher since charge rejection of anionic organics from the anion-exchange membrane would be minimal. There is also a significant issue surrounding progressive dilution of acid, due to recycle losses. However, just as in CR, this can be offset by supplementing with fresh acid.

#### 4.2.4. ELECTRODIALYSIS

Thermodynamically driven ion-exchange processes such as Donnan membranes, LIE, and resins show potential for CR because they are charge-selective and resilient to fouling. However, the kinetics of exchange decrease as thermodynamic equilibrium is reached, making high yields and fast kinetics mutually exclusive. To compensate for this, greater media volumes

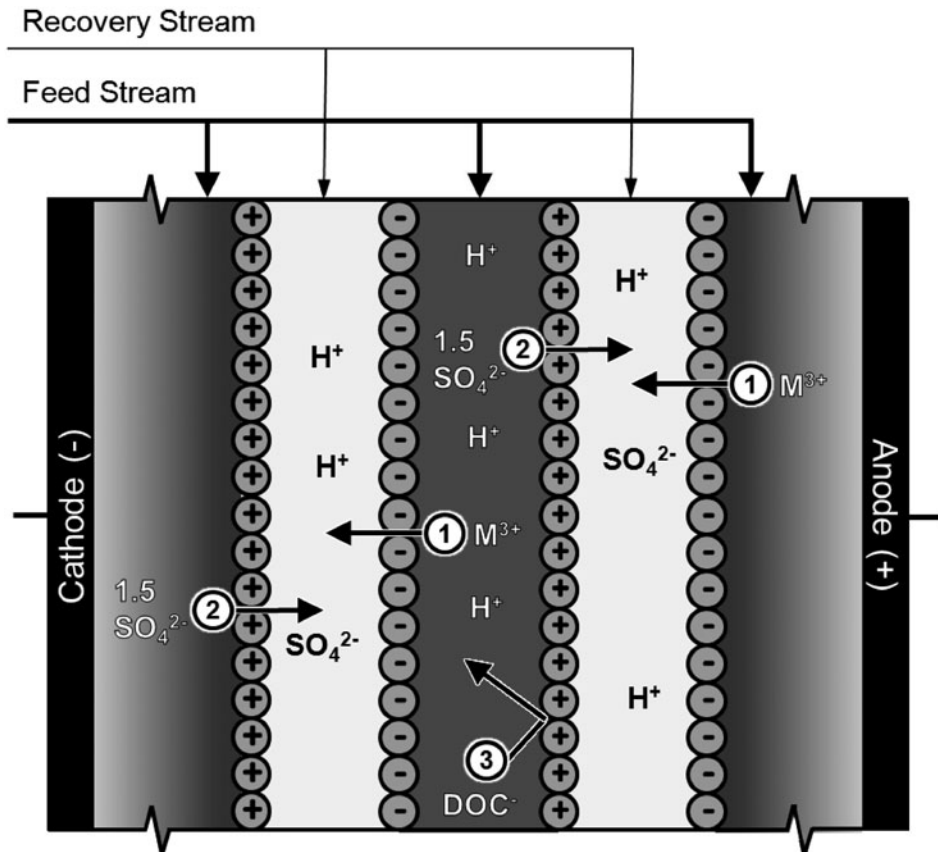
or membrane areas are required to provide sufficient capacity at full scale. Active processes such as electrodialysis (ED) may allow the same advantages of ion-selective processes but greater control over the process kinetics and process costs, by being able to control kinetics independently of yields (through the applied potential).

ED has not been tested for CR but is a well-established concept in the recovery of cations (nickel, copper, aluminum, and acid) in the electroplating and anodizing industries (Lancy and Kruse, 1973; Itoi et al., 1980; Franken, 2003; Agrawal and Sahu, 2009). ED has been employed to create closed-loop electroplating processes which offer similar reductions in waste and chemical requirements to CR. To do this, electric current is applied across stacks of cells containing acidified solutions of metals, forcing the movement of cations through cation-selective membranes towards the anode and away from immobile and anionic contaminants (Figure 4).

Metal recovery yields in excess of 90% have been reported using ED, though recoveries diminish with increasing feed concentration (Itoi et al., 1980). Concerns arise over membrane fouling due to organic compounds and anode scaling due to aluminum hydroxide. However, ED reversal, pulsing, and cleaning have been implemented to control fouling when analogous streams are treated with ED (Lee et al., 2002, 2003; Strathmann, 2010). Using these methods, successful ED treatment of aluminum-containing solutions has been documented, although with a focus on acid rather than metal recovery (Franken, 2003). ED-based processes have also been used to desalt organic-rich fermentation broths, demonstrating that the problem of organic fouling can be managed (Lee et al., 2003).

The fundamental challenge for ED recovery is energy consumption. If fouling can be controlled, the high concentrations of ions will reduce the resistance of the WTR stream compared to conventional ED feeds, such as brackish water. However, a far greater amount of ions require transportation for ED applied to WTR and, as Faradaic principles govern the process, the minimum electricity requirement and cost can be accurately predicted (Audinos, 1986). Using these principles and chemical prices, the overall cost of CR using ED can be calculated. For alum, the cost of recovery equals the value of coagulant recovered, and for ferric the cost exceeds the value recovered (Keeley et al., 2012). Selectivity and recovered coagulant purity are likely to be comparable to those of dialysis processes that use similar ion-exchange membranes (Prakash and Sengupta, 2003). The combination of a predictable high energy demand and the unknown extent of fouling and scaling have left ED CR at the conceptual stage of development.

Acid recovery is readily achievable with ED, with the use of less porous ion-exchange membranes allowing rejection of multivalent cations but permeation of protons. When ion complexation is minimized, acid recoveries above 90% can be achieved (Pierard et al., 2002). ED acid recovery has also been achieved simultaneously with metal recovery, with acid yields of



**FIGURE 4.** Theorized electro-dialysis recovery of trivalent coagulant metals. 1. Trivalent coagulant metals move from the acidified feed, towards the cathode, until their path is blocked by an anion-selective membrane. 2. Acid/coagulant counterions move from the acidified feed, towards the anode, until their path is blocked by a cation-selective membrane. 3. Despite having the correct charge, organic material in the feed is rejected by the membrane due to its bulk.

66–72% and nickel losses of 4% (Xu and Yang, 2004). However, acid recovery from CR residuals is subject to the same potential problems as CR itself, i.e., fouling, scaling, and energy demand.

## 5. COAGULANT RECYCLING IN WW TREATMENT

As previously highlighted, coagulant reuse in potable treatment is challenged by numerous regulatory and economic issues. Although coagulant dosing in WW treatment is less prevalent than in potable water production, demand is growing in response to tighter final effluent consents and it remains a practical target for recovered coagulant reuse. The absence of DBP limits and

less stringent heavy metal regulations reduce the requirement for coagulant-contaminant separation, commensurately lowering both recovery costs and the risk of failing quality regulations.

Coagulant can be recovered for reuse from both WW and potable sludges. Alum was recovered from primary WW sludge with a yield of 70% at a pH of 2 (Jimenez et al., 2007). The recovered coagulant not only performed comparably to fresh coagulant (when supplemented with 30% fresh material) but also reduced residual sludge volume and mass by 45% and 63%, respectively. The study was only partly successful in its aim to inactivate helminth ova in the insoluble sludge fraction to enable the residual sludge to meet agricultural standards for application to crops for human consumption. For this, further stabilization with lime would be required (Jimenez et al., 2007).

The acid requirement was found to correspond to the stoichiometric dose. Addition of acid beyond this solubilized no more aluminum. This is contrary to what might be expected for WW sludge which has higher alkalinity levels (Slechts and Culp, 1967) but was explained by a low WW pH of 5, indicating minimal buffering capacity (Jimenez et al., 2007). The study also found that increased solids above 5.9% in the sludge feed led to reduced recovery efficiencies at the mixing conditions and duration tested. This suggests that mass transfer becomes a key consideration when acidifying thicker sludges. This parameter will need to be balanced with the cost of transporting WTR, which would benefit from the highest possible sludge thickness to minimize volume.

Other studies have examined the effect of dosing acidified and raw WTRs to WW. Jar tests examining total orthophosphate removal from a synthetic WW containing 10 mg/L as P required a dose of 75 mg/L Al with unacidified alum sludge and only 15 mg/L Al with fresh alum. The same dose of unacidified sludge also removed 40–60% total phosphorus and 35–40% COD from two different municipal WTs (Table 6). This performance data could be used to estimate the benefit of direct WTR disposal to sewers, which is poorly documented but practiced widely (Figure 1).

While dosing of unacidified WTRs enhances treatment, prior regeneration of the constituent coagulants with acid improves removals of solids, COD, and phosphorus by a further 20–30% at much lower doses (Table 6). Under these circumstances, recovered alum matches commercial alum performance at equal doses, in terms of removal of solids, COD, and phosphorus (Table 6). This performance was maintained for the coagulant recovered from the WW sludge even after four cycles (Xu et al., 2009a). The same study reported that potable sludge provided no performance advantages over that from WW, such that transporting of sludge from potable to WW sites could be unnecessary, although doing so would provide a plentiful source of recovered coagulants. Recovered, unfiltered ferric coagulants compared less favorably with commercial equivalents, particularly for solids removal. Filtering the recovered ferric coagulant improved solids and COD removal (the

**TABLE 6.** A comparison of commercial and recovered coagulants in wastewater treatment

| Sludge type and dose (mg/L as Al or Fe) | Alum              |                                      |                            |                 | Ferric                     |                  |
|---|-------------------|--------------------------------------|----------------------------|-----------------|----------------------------|------------------|
|   | 4                 | Nonacidified<br>75                   | Commercial<br>30           | Recovered<br>30 | Commercial<br>30           | Recovered*<br>30 |
| Removals                                |                   |                                      |                            |                 |                            |                  |
| SS (%)                                  |                   |                                      | 97                         | 97              | 90                         | 25 (67)          |
| COD (%)                                 | 53                | 35–40                                | 62                         | 62              | 48                         | 55               |
| Soluble P (%)                           |                   |                                      | 96                         | 99              | 95                         | 81 (66)          |
| Total P (%)                             | 95                | 40–60                                |                            |                 |                            |                  |
| References                              | Xu et al. (2009a) | Georgantas and Grigoriopoulou (2005) | Parsons and Daniels (1999) |                 | Parsons and Daniels (1999) |                  |

\*Values in parentheses denote removals when neutralized.

latter to beyond commercial coagulant levels) but to the detriment of phosphorus removal (Parsons and Daniels, 1999; Table 6).

CR in WW shows great promise by offering greater economic rewards than bulk reuse strategies, by reducing demand for fresh coagulant. Although purification stages have been shown to improve recovered coagulant performance, the less strict WW quality regulations permit less expensive, unselective technologies such as simple acidification. Further work is required to ascertain the effects of sludge acidification on anaerobic digestion, since biogas production and energy offsetting are key objectives in WW treatment and their potential impairment by CR would jeopardize its acceptance by the industry. The particular concerns are the low pH (and possible requirement of neutralization) and the accumulation of heavy metals and aluminum, which have been shown to potentially inhibit anaerobic digestion (Chen et al., 2008). Using recovered potable coagulants in WW treatment would negate the need to acidify WW sludge and may prevent many of these potential problems for AD. However, even if CR is successful in the context of WW, it would not fully solve the problems of coagulant demand in potable treatment.

## 6. DISCUSSION

There is a wide range of technologies available that may be considered for CR, each with advantages and disadvantages, as highlighted by SWOT analysis (Table 7). Most of these are capable of consistently recovering >70% of coagulant metals and reducing sludge volumes by 60%. These levels of recovery performance would allow significant improvements to water treatment sustainability and partial fulfillment of many of the principles of green

**TABLE 7.** A performance summary and SWOT analysis of key coagulant recovery options

| Recovery approach            | Typical recovery performance |                              |                  |   | Strengths   | Weaknesses  | Opportunities (common to all)   | Threats (common to all)                                | References |
|------------------------------|------------------------------|------------------------------|------------------|---|---|---|---|--|------------|
|                              | M <sup>3+</sup> yield (%)    | M <sup>3+</sup> conc. (mg/L) | DOC conc. (mg/L) | DOC conc. (mg/L)  |   |   |   |  |            |
| Simple acid solubilization   | 90                           | 2,500                        | 500              | Simple, low cost, relatively well understood                                      | Nonselective, heavy metal and organic compound contamination                        | Developments in other fields that can be transferred to GR. | Increased acid and alkali costs relative to commercial coagulants                             | Saunders and Roder (1991) and King et al. (1975)       |            |
| Simple alkali solubilization | 80                           | 950                          | Higher than acid | Simple, rejects heavy metals  | Higher cost, specific to alum, low recovery concentrations, worse DOC contamination | Increased commercial coagulant prices                       | More stringent treated water and coagulant quality regulations                                | Masschelein et al. (1985), and Isaac and Vahidi (1961) |            |
| Ultrafiltration              | 80                           | 560                          | 75               | Relatively selective, low cost and well understood technology                     | Considerable organic compound permeation and fouling                                | Decreased commercial coagulant quality                      | Competition from alternative reuse options  | Lindsey and Tongkasame (1975)                          |            |
| ReA/ process                 | 85                           | 12,500                       | <2               | Capable of recovering very pure and concentrated alum                             | Multistage approach elevates costs and complexity                                   | Increased landfill costs                                    | Diminished raw water quality placing greater stress on metal-contaminant separation processes | Ulmert and Sarner (2005)                               |            |
| Liquid ion exchange          | 90                           | 30,000                       | —                | Allows high concentrations to be achieved in the stripping stage, quite selective | Risk of toxic solvent carryover, and process complexity                             | More stringent landfill regulations                         |   | Westerhoff and Cornwell (1978), and Cornwell (1979)    |            |

|                        |    |       |             |  |   |                             |
|------------------------|----|-------|-------------|--|---|-----------------------------|
| Cation exchange resins | 95 | 5,000 | —           | Capable of high yields and purity  | Regeneration is inefficient and costly.<br>Problems with scale-up                                       | Petruzzelli et al. (2000)   |
| Anion exchange resins  | 90 | —     | 60% removal | Potential to reduce organic contaminant levels in other processes                    | Inadequate performance to stand alone, adds complexity when used as a polishing stage                   | Anderson and Kolarik (1994) |
| Donnan membranes       | 80 | 4,700 | 17          | Robust performance in terms of purity and concentration                              | Slow kinetics require large membrane areas or contact time, harming process economics                   | Prakash and Sengupta (2004) |
| Electrodialysis        | —  | —     | —           | May be able to accelerate the slow kinetics of other ion exchange membrane processes | Poorly understood in this role and likely to face problems with fouling, scaling and high energy demand | —                           |

(Continued on next page)



**TABLE 7.** A performance summary and SWOT analysis of key coagulant recovery options (*Continued*)

|                      |   |   |   |  |   |
|----------------------|---|---|---|--|---|
| Dosing to wastewater | — | — | — | <p>Bypasses many of the quality issues faced in potable CR while still yielding significant treatment benefits</p> <p>Fails to solve the problem of coagulant demand at potable works. Recovered coagulant transport between sites is dependent on proximity</p> | <p>Babatunde and Zhao (2007) and Parsons and Daniels (1999)</p> |
|----------------------|---|---|---|--|---|

chemistry, as set out in the “Introduction” section (Anastas and Warner, 1998). CR technologies broadly fulfill these principles in terms of waste reduction, atom economy, and a movement towards using coagulants as nonconsumable catalysts. The key shortfalls of CR in these terms are: incomplete recovery (~30% is lost), the use of concentrated acid, electricity usage, and the risk of elevated DBPs. Reuse of WTRs in WW treatment could nullify many of these shortfalls, including use of acid but at the cost of less complete atom economy and recycling efficiency.

The recovery technologies investigated have reported a wide range of selectivity and process complexity. Ion exchange has shown the highest degree of recovered coagulant purification but at a cost that is currently unrealistic at full scale (Table 8). Pressure-filtration recovery of alum shows potential to reduce operating costs when compared to conventional practice but is yet to demonstrate adequate selectivity. Even the most selective technology, the Donnan membrane process, has been shown variable purity in response to differing feed sludge DOC loadings. Reliance on a single separation stage leaves recovered coagulant purity vulnerable to variability of raw water quality. This has been alleviated by multistage separation (such as the *ReAl* process) but to the likely detriment of process economics, which are already critical for more basic CR technologies (Table 8). Furthermore, technology transfer into CR is restricted by the low value of ferric and alum compared to the high-value metals commonly recovered in other industries using similar processes.

Although the approaches are diverse, the common challenge for potable reuse is achieving a high level of contaminant rejection without incurring excessive costs. The literature has shown (highlighted in Tables 7 and 8) that these two aims are mutually exclusive, with current prices and technology. It is only when recovery costs change, in relation to coagulant prices, that potable reuse of recovered coagulant can be considered a viable option.

Available literature for CR has also shown a disparity between apparent promise in short-term lab-scale trials and process reliability at full scale, with full-scale CR's initial successes being better documented than ultimate failures. A few available accounts of failed full-scale CR operation give only a qualitative indication of the circumstances that lead to process failure (e.g., diminished raw water quality, problematic sludge handling, and marginal economic benefit). Although of some use, the lack of quantitative data highlights a knowledge gap that must be filled before any CR technology can be operated reliably and safely at full scale. It may be that the cause of failure in recovered coagulant quality is discrete, predictable, and detectable. For instance, if raw water DOC or heavy metal loadings exceed a certain level, CR systems could then be paused, mitigating the risk of quality failures. This more reactive approach is likely to be more economic than investing in CR capable of meeting quality standards under all conditions.

**TABLE 8.** A Comparison of operating costs for key coagulant reuse options against conventional coagulant dosing practice

| Coagulant operating costs as £/1,000 mols of M <sup>3+</sup> recovered or purchased | Pressure filtration | Donnan dialysis | Electrodialysis | Dosing to WW | Conventional practice |        |
|---|---------------------|-----------------|-----------------|--------------|-----------------------|--------|
|   |                     |                 |                 |              | Alum                  | Ferric |
| Solubilization acid   | 20                  | 20              | 36              | 20           |                       |        |
| Recovery chemicals (cleaning chemicals <sup>a</sup> , dialysis acid)                | 2                   | 20              | 2               |              |                       |        |
| Electricity   | 3                   |                 | 8               |              |                       |        |
| Membranes <sup>b</sup>  | 26                  | 34              | 11              |              |                       |        |
| Landfill gate fees <sup>c</sup>   | 10                  | 10              | 10              | 10           | 20                    | 20     |
| Intersite transport <sup>d</sup>  |                     |                 |                 | 20           |                       |        |
| Commercial coagulant  |                     |                 |                 |              | 60                    | 35     |
| Total   | 61                  | 84              | 67              | 50           | 80                    | 55     |

Adapted from current prices and published performance data as listed in Keeley et al. (2012), unless stated otherwise:

- a) Estimated to be 3% of total operating costs (Verrecht et al., 2010)
- b) Considered as a consumable
- c) Including neutralization to moderate pH, if required. Excluding transport costs.
- d) Based on transporting 20% DS WTRs to a WWTP 20 miles away, in 30 tonne loads, using fuel consumption data from Coyle (2007)

**TABLE 9.** Coagulant markets and price dynamics

| Coagulant           | North American market share (%) | Average US price increase 2008–2009 (%) <sup>1</sup> | Average UK price increase 2008–2009 (%) <sup>2</sup> | Cost drivers (coagulant type affected, in parentheses)   |
|---------------------|---------------------------------|--|--|--|
| Aluminum coagulants | 20–25                           | 14–51  | 5–18   | Fuel (universal)<br>Bauxite (alum)<br>Sulfuric acid (alum)<br>Aluminum trihydrate (PACI*)<br>Aluminum metal (ACH <sup>†</sup> )<br>Hydrochloric acid; chlorine (PACI, ACH) |
| Ferric chloride     | 10–15                           | 22   | N/A  | Scrap steel/pickle liquors<br>Hydrochloric acid; chlorine  |
| Ferric sulfate      | 10–15                           | 40   | 13   | Sulfuric acid<br>Iron ore  |

Adapted from Henderson et al. (2009); <sup>1</sup>Association of Metropolitan Water Agencies (AMWA) survey with 42 responses from water utilities; <sup>2</sup>AMWA survey with seven responses from water utilities (Walsh, 2009).  
\*Poly aluminum chloride, <sup>†</sup>Aluminum chlorohydrate

While important, CR and engineered solutions are not the only means for improving coagulant management: supply-side forces must be understood, anticipated, and mitigated. The widespread use of coagulation in water treatment has made the industry reliant on the supply of coagulants. The dynamics of coagulant supply are complex and often poorly understood by water utilities. Previous near misses in supply integrity and price rises have not been predicted by the utilities (Henderson et al., 2009). A significant attraction of CR is its potential to reduce dependence on external market forces, though there will always be a requirement for some fresh coagulants.

Commodity chemicals such as alum and ferric are often sourced from only a few distributors, weakening the utilities' market position. On an international scale, coagulant supply and prices are affected by global economic conditions. As shown in a comprehensive study by the Water Research Foundation (Table 9), coagulant supply is dependent on the supply and prices of many other commodities (Henderson et al., 2009). The study notes that many raw chemicals involved in coagulant manufacture are demanded by competing industries which often dwarf the market share and power of the water industry (e.g., manufacturing and construction for iron and aluminum, and the production of fertilizer uses 60% of the total of sulfuric acid produced). The impact of these dominant and competing industries on commodity markets is passed onto the market price for coagulants, causing them to inflate with global economic growth. This is particularly true for fuel prices

**TABLE 10.** US Producer Price Indices (PPI) for commodities related to water treatment

| Commodity                   | Base year (PPI = 100) | PPI in January 2012 |
|-----------------------------|-----------------------|---------------------|
| All industrial commodities  | 1982                  | 201                 |
| Water-treating compounds    | 1985                  | 191                 |
| Sulfuric acid               | 1987                  | 165                 |
| Petroleum products, refined | 1982                  | 294                 |
| Basic inorganic chemicals   | 1982                  | 339                 |
| Iron and steel              | 1982                  | 257                 |
| Nonferrous metals           | 1982                  | 254                 |

Adapted from Bureau of Labor Statistics (2012)

and transport costs, which for coagulants bearing a low value to mass account for a significant contribution to the overall cost.

Other coagulant raw materials are sourced as by- or coproducts from other processes, further diminishing the utilities' market control. Metal chloride coagulants are particularly dependent on the availability of waste pickle liquors from metal finishing industries. Hydrochloric acid is another key commodity for coagulant production, and its price is a function of chlorine. The supply of chlorine is related to the demand for its coproduct sodium hydroxide in the energy-intensive chlor-alkali process (Henderson et al., 2009).

Complex and interlinked markets are a challenge to predict accurately but the disruption caused by supply fluctuations can be alleviated by flexible usage strategy. Reliance on a single coagulant type or supplier can leave water utilities vulnerable to external market forces, with shortages posing a risk to water treatment capacity, quality, and cost (Henderson et al., 2009). As the changes in commodity prices illustrate, all commodities have experienced price inflation over the last 30 years but some more than others (Table 10).

Long-term flexibility in coagulant dosing strategy has allowed water utilities to avoid the most inflation-afflicted commodities by switching coagulant types. This is demonstrated by the producer price index for water-treating compounds rising significantly less than inorganic chemical and metal price indices would suggest. CR would allow even greater flexibility and a shift of reliance from coagulants to sulfuric acid, which has historically been less prone to inflation (Table 10). Increasing demand for coagulants, in response to more widespread restrictions on final effluent consents for phosphorus, is likely to put further inflationary pressure on prices in Europe, in the coming years (European Commission, 2000). Transporting WTRs to wastewater treatment plants (WWTPs) for phosphorus removal would offset coagulant demand, without having to negotiate the stringent DBP regulations of potable reuse. This will reduce costs (Table 8) and secure fresh coagulant supply for the role its purity is most valuable in: potable treatment.

When discussing price changes, it is also important to remember the relative volumes of chemicals used. For CR, the cost of sulfuric acid required

to regenerate coagulant, in relation to the cost of equivalent virgin coagulant, is between 30% and 60% for alum and >60% for ferric (Keeley et al., 2012)—demonstrating the impediment to CR implementation at full scale by the relatively low cost of coagulant (USEPA, 2011). The development of novel, high-performance zirconium-based coagulants (Jarvis et al., 2012), with increased value relative to recovery costs, may improve the economics of CR.

A holistic approach is also required when considering the CR residuals. Acid recovery and recycling would reduce waste acidity, allowing easier disposal and reduced demand for virgin acid and reducing process costs to help drive CR towards better fulfilling the principles of green chemistry. In pure economic terms, acid recovery alongside CR appears to be highly beneficial, though acid recovery is itself subject to efficiency limitations. As with CR, acid recovery operations add complexity and capital costs that will be further obstacles to CR implementation.

Potable regulations will play an important role in the success and failure of CR for reuse. British Standards have been developed with commercial coagulants in mind, leaving the targets for CR purity uncertain. The USEPA approach of allowing no more than a 10% contribution from treatment chemicals to regulated parameters seems more pragmatic. If a low level of DOC contamination in recovered coagulant proves to have no effect on treated water quality, a regulatory focus solely on final treated water quality may encourage CR. Current standards allow an insufficient margin of error for existing CR technologies, making the risks of failure outweigh the benefits in cost savings.

However, it would be naïve to assume regulations will change to facilitate the potential sustainability benefits of CR. Public health and trust are the foremost priorities of potable treatment, and quality regulations are designed to enforce this philosophy. While water utilities are obliged to minimize costs and protect the environment, these cannot be at the expense of risk to public health. Only a few of the many known DBPs are currently regulated, and more comprehensive regulations are expected in the future. This implies that CR processes must be developed not only to offer better value than conventional coagulation practice but also to offer consistently better treatment quality. The extent to which recovered coagulant contaminant levels and treated water quality are linked must be determined. A thorough understanding of this relationship will allow the minimum recovery cost to be balanced with the requirements of modern potable treatment.

Coagulant reuse strategies besides potable treatment should also be considered. While direct recycling of coagulant from WTRs for potable treatment may be the most complete form of reuse, the economic implications of meeting regulated quality standards currently make nonpotable reuse of recovered coagulants and WTRs more achievable. In this respect, dosing recovered coagulant at WWTPs seems particularly promising in the short

term, subject to favorable logistical conditions. Such practices would allow sustainable disposal of WTRs and reduce fresh coagulant demand for WW treatment but still fall short of reducing net-chemical demand in potable treatment itself.

## 7. CONCLUSIONS AND RESEARCH NEEDS

Currently, potable reuse of recovered coagulant is not at a stage where it can be implemented at full scale. Its ability to recover coagulant at sufficient purity and costs has been demonstrated individually with different technologies but not simultaneously. Current regulations and prices continue to make the risk of implementing CR outweigh the potential benefits; fresh coagulants remain the best-value, lowest-risk solution. If the economics and selectivity of recovery can be improved or if market forces increase the cost of coagulants, in relation to recovery costs, then it may become viable. Research is required in the following areas to better understand and mitigate the process costs and risks:

- Effective acid recovery
- Improving ion-exchange performance in terms of exchange rates and selectivity
- The potential and costs of successive polishing stages, after less selective processes such as pressure filtration

Holistic research approaches will also improve the viability of CR for potable reuse:

- Identifying the impact of site raw water characteristics on CR quality
- Negotiation with regulators with regard to recovered coagulant and their requirements for coagulant purity or actual impact on treated water quality

In contrast, the application of recovered coagulant in WW shows immediate promise. While it does not fully meet the ambitions of green technology and zero net chemical usage in potable treatment, it does provide a disposal route for WTRs and reduces external demand for coagulant (which will help secure coagulant supply and prices for potable treatment). The comparatively lenient requirements of WW treatment allow nonselective and frugal recovery methods, minimizing regulatory and economic risks. Provided logistical conditions are favorable (which must be verified on a case-by-case basis), it is advisable that this is the focus of future research and trials. The key research needs in these terms are as follows:

- Ascertaining the optimum logistical configuration to transport and acidify WTRs to WWTPs
- The cost-benefit of acidifying WTR prior to dosing to WW
- The impact-recovered coagulants have on downstream WW processes, in comparison to commercial alternatives. There are specific concerns with regard to their effect on AD biogas production, metals loadings in digestate, and residual metals in final effluent

This study has systematically examined the aims and benefits of CR, against the technological and economic environment the water industry currently faces. This has allowed the limitations of CR to be identified and thus the reuse strategy that offers the greatest benefit, in terms of green technology, economics, and operational risk.

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