Recovery of Inorganic Compounds from Spent Alkaline Pulping Liquor by Eutectic Freeze Crystallization and Supporting Unit Operations: A Review

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After the kraft or soda pulping of lignocellulosic materials to produce pulp suitable for papermaking, the spent pulping liquor typically has been recovered by multi-effect evaporation, followed by incineration in a recovery boiler. This review article considers one unit operation, eutectic freeze crystallization (EFC), that may have potential to save some of the energy that is presently consumed in the evaporation step during recovery of inorganic chemicals from spent pulping liquor. Based on a review of the literature it appears that EFC can be employed to obtain relatively pure sodium sulfate and sodium carbonate, along with relatively pure water (in the form of ice) from the spent liquor, under the assumption that lignin previously has been removed by acidification and precipitation. Issues of inorganic scale formation, during the operation of an EFC process applied to lignin-free black liquor, will require research attention. The chemical reactions to regenerate the active pulping chemicals sodium hydroxide and sodium sulfide from sodium carbonate, sodium sulfate, and other compounds isolated by EFC can be carried out either in a separate operation or by returning the materials to the feed of an existing recovery boiler.

Keywords: Kidney technologies; Pollution abatement; Black liquor; Sodium sulfate; Sodium carbonate; Indirect cooling crystallization; Incremental pulp mill capacity; Replacing the recovery boiler

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INTRODUCTION

Since about 1930 the pulp and paper industry has relied heavily on a process of evaporative concentration of spent pulping liquor followed by incineration under reducing conditions and recausticizing as a means of recovering pulping chemicals (Sjöström 1993; Bajpai 2017). The primary purpose of chemical pulping is to remove lignin from the woody material. As has been detailed in standard texts and review papers, the delignification can greatly enhance the value of the resulting fibers (Biermann 1996; Tikka 2008; Fardim and Tikka 2011). Chemical breakdown and dissolution of the lignin permits the fibers to be separated from wood without major damage or loss of fiber length. The pulped fibers generally have greater conformability, collapsibility (to form ribbon-like shapes), and more hydrophilic character of the surfaces, all of which contribute to stronger inter-fiber bonding (Young 1994; Fardim and Tikka 2011). The lignin-free fibers generally also have a more stable appearance, and they can be bleached to a high brightness with little tendency of yellowing (Dence and Reeve 1996; Suess 2010). In addition, delignified fibers can contribute superior absorbency to tissue, toweling, and highly absorbent disposable products (Parham and Hergert 1980; Lund *et al.* 2012; Hubbe *et al.* 2013).

The classical kraft recovery cycle, which depends on evaporation of water from spent pulping liquor (Venkatesh and Nguyen 1992), has been employed throughout the world as the primary means of converting spent pulping liquor back to its active form, suitable for reuse in the pulping process (Grace 1992; Empie 2009; Bajpai 2017). The capacity of a single recovery boiler can be as high as 6000 metric tons of dry solids in a 24 hour period (Haaga and Laitinen 2002). Parrish (1998) describes a range from about 340 (“small”) to 2700 (“large”) metric tons black liquor solids per day. Such a recovery cycle, in its time, has provided many advantages. The heat from the burning of low-valued lignin byproducts and some hemicellulose degradation products in the spent pulping liquor is used to supply the energy needed to evaporate water from the spent pulping liquor (Tikka 2008). Excess steam can be used for the drying process on paper machines. The conditions within the furnace can be controlled such that the sodium sulfate is reduced to sodium sulfide. Sodium carbonate within the mixture can be converted to sodium hydroxide by addition of lime (CaO), the active form of which is later recovered by use of a lime kiln (Venkatesh 1992; Tikka 2008; Empie 2009; Bajpai 2017).

In this article the term “recovery boiler” will be used when referring to the furnace, since the heat generated by the combustion of lignin and other organic materials is used to generate steam, which can then be used as a power source. Despite the many advantages and high level of maturity of kraft recovery technology, there are several reasons for the paper industry to consider either supplementing or replacing the recovery boiler and associated processes with something else. These reasons fall into the categories of hazards, capital expenses, operating expenses and problems, and the energy footprint. Recovery boiler explosions, though infrequent, cause major disruptions and sometimes loss of life when they occur at facilities throughout the world (Grace 1986; Burelle *et al.* 2016). Empie (2009) notes that there was an average of about two smelt-water explosions per year, somewhere in the world, during the period 1970 to 1995. A new recovery system of economically viable size can cost in the range of about 100 million to a billion dollars (Brewster 2007; Empie 2009; ETSAP 2015). Operation of such a system can have major expenses associated with corrosion of the high-grade metal tubing used to convert heat energy into steam (Singbeil and Garner 1989). The potential for severe scaling discourages the implementation of recovery boiler use in the pulping of such lignocellulose resources as bamboo and straw due to their relatively high content of silica (Hammett *et al.* 2001; Tutus and Eroglu 2003; Pekarović *et al.* 2006; Bajpai 2017). Evaporative removal of water, as used in the conventional kraft recovery technology, also has a relatively high energy footprint (Fernández-Torres *et al.* 2012); in other words, the usage of heat energy to evaporate water from pulping liquor can be regarded as wasteful based on current concepts of life cycle analysis. Alternatively, there is potential to employ EFC technology as a kind of kidney, selectively removing certain inorganic compounds while returning desirable inorganic compounds such as sodium sulfate to the recovery boiler system.

EUTECTIC FREEZE CRYSTALLIZATION

History

Among the technologies having potential to replace the evaporative concentration of black liquor, in the recovery system for kraft pulping, this review article focuses on eutectic freeze crystallization (EFC). The phase change from water to ice requires only about 15% as much energy as the corresponding transformation of water to steam (Osborne 1939; Osborne *et al.* 1939). Water's heat of fusion (at zero ºC) is 6.00 kJ/mole, whereas its heat of evaporation (at 100 ºC) is 40.65 kJ/mol. To put these numbers into perspective, the energy to raise the temperature of water from 0 to 100 ºC is 7.54 kJ/mole. Somewhat higher heat amounts are needed to change the temperature of salt solutions, depending on the details of their composition (Magalhaes *et al.* 2002). Even when taking into account such issues as inefficiencies of refrigeration processes and the need to cool hot water to the freezing point, there is clearly a motivation to consider EFC as a means of separating water from various industrial process water streams. When water freezes, the crystals tend to exclude impurities (Terwilliger and Dizio 1970; Stepakoff *et al.* 1974; Hasan and Louhi-Kultanen 2016; Szpaczynski *et al.* 2017). When saturated solutions of various compounds are super-cooled to a moderate degree, two solid phases – ice and an inorganic compound – will separate out of solution simultaneously. In a suitably designed device, the ice floats and the inorganic crystals settle, leaving behind an aqueous solution that is concentrated in ions associated with more-soluble inorganic compounds and also more concentrated in any organic compounds present in the initial mixture. In broad terms, EFC has been considered for treatment of relatively concentrated solutions, such as salty brines and the retentates from reverse osmosis membrane processes.

Though there is a real advantage, in terms of energy, when employing freezing rather than evaporation as a means to remove water from black liquor, it is important that such an advantage should not be over-stated. Typical evaporation systems are arranged as a series of about five to seven "effects", each of which removes a corresponding portion of the water from the mixture (Tikka 2008; Bajpai 2017). A lot of the energy is saved because the water vapor obtained from black liquor evaporation in each effect is used as a heat source and recondensed at the subsequent effect. According to Bajpai (2017), one unit of steam is employed to evaporate 0.7 to 0.9 mass units of water in each effect. The overall economy, with about six units in series, has been estimated to be about 4.5 to 5 units of water evaporated per unit mass of steam (Tikka 2008; Empie 2009), though lower values (perhaps 3.6 to 3.8) may be more realistic. A variety of pumps and vacuum systems, all of which use power, have to be run in order to operate such an evaporator system. In the case of EFC, related cost-savings are possible too, since the ice can be allowed to melt in order to bring down the temperature of the stream entering the EFC system (Gerbasi *et al.* 1993). On the negative side, there can be inefficiencies associated with the needed cooling systems for EFC. The presence of impurities can lower the operating temperature, which may increase costs. Another concern is that an EFC process generally uses electrical energy, whereas the conventional kraft recovery process uses incineration of renewable organic matter as the main energy source. Based on the values given above, one still can expect a large energy advantage when using EFC in place of evaporative concentration before a recovery boiler. However, a detailed energy analysis of an optimized EFC system is needed, with an integrated strategy of heat recovery, and the results should be compared to a corresponding analysis for a typical 6-effect evaporator system for black liquor.

An early investigation of EFC was reported by Pangborn (1963), who showed that a combination of slow cooling and seeding with crystals was able to separate salt solutions into two solid phases – salt and relatively pure water. Stepakoff *et al.* (1974) showed that the EFC process could be optimized by initially separating just ice, until the eutectic point was reached, at which point both the salt and the water were at the point of incipient generation of new crystals from solution. Thereafter, conditions were optimized for more gradual isolation of ice and salt, followed by their gravity separation and washing. Barduhn and Manudhane (1979) showed that the EFC process could be optimized and run in a continuous manner. Advances in equipment by van der Ham *et al.* (1999) and Rodriguez-Pascal *et al.* (2010) achieved more efficient gravitational separation of the ice and salt crystals, since the ice tends to float due to its low density, and the inorganic compounds tend to settle, due to their higher density.

Applications of EFC

Application areas for which the EFC technology may be especially well suited appear to include not only spent pulping liquors from paper manufacturing, which will be the focus of this article, but also the handling of brines from reverse osmosis and ion exchange operations. Though it has been proposed to dispose of such brines by deep-well injection (Barduhn and Manudhane 1979; Afrasiabi and Shahbazali 2011; Kim 2011), such practices are wasteful of resources, expensive, and have the potential to cause contamination of groundwater. Desalination, which is widely practiced as a means of obtaining fresh water in arid regions, can benefit from EFC technology because the salt can be obtained as a relatively pure byproduct (Afrasiabi and Shahbazali 2011; Reddy *et al.* 2010). If the saline brine were merely discharged into the ocean, it would disrupt local salinity levels and interfere with marine life (Kwon and Yoon 2017). Contaminated brines from either reverse osmosis concentration or ion exchange treatment of industrial effluent streams have also been treated, at a research level, using EFC (Cob *et al.* 2014). Also, EFC can be used for the isolation of various chemical compounds (Chowdhury 1988).

For freeze-concentration in general, the most prominent industrial usage appears to be in the food industry (Liu *et al.* 1997; Aider and de Halleux 2009; Petzold and Aguilera 2009). In such applications the product has relatively high value, and the cold temperatures tend to minimize any decomposition. However, such systems do not involve eutectic mixtures, and no salts are precipitated from solution.

Some recent review articles dealing with the end-processing of brines either have mentioned EFC only briefly (Burbano and Brankhuber 2012; Subramani and Jacangelo 2014; Giwa *et al.* 2017; Tsai *et al.* 2017) or not at all (Khawaji *et al.* 2008; Elimelech and Phillip 2011; Kim *et al.* 2011; Morillo *et al.* 2014). Wiegandt and von Berg (1980) have attributed a lack of attention to freezing technologies to the widespread promotion of alternative technologies, for which more information has been provided to potential users. Chowdhury (1988) attributed the lack of investment in freeze concentration to capital costs, which were said to be as much as three times higher than simple evaporation and other crystallization techniques. Pronk *et al.* (2006) mentioned high operating costs in addition to capital costs. However, recently there have been reports of large-scale implementation of EFC (Creamer 2016; Chambers 2017; Lewis 2017, 2018; Steenkamp 2017). Therefore, in light of the high costs of conventional chemical recovery system for spent pulping liquors, the capital costs of EFC need to be evaluated.

Basic Principles of EFC

Theory related to the main steps of supersaturation, nucleation (where nuclei are born) and growth of crystals in solution has been reviewed (Mullin 2001; Lewis *et al.* 2015). The term supersaturation can be defined as a situation in which the solubility product of a specific mineral (*e.g.* NaCl) exceeds the value at which the crystal is known to be capable of being present as a solid phase. In industrial practice, a condition of supersaturation can be achieved by removal of water from a solution, *e.g.* by evaporation or other means. Nucleation means that new crystals appear, either due to high enough supersaturation, due to the nucleating effects of shear or surfaces, or in many cases due to the intentional feeding of “seed” crystals that match the composition and crystal habit of the desired product. The term crystallization, in the context of inorganic ionic matter, means that, although there may be imperfections, the substances that come out of solution are expected to be arranged in a highly regular pattern, often dictated by the sizes of the positive and negative ions that compose the compound. Finally, the term growth implies that material from the solution phase continually migrates to the surface of the solid particles, relieving the condition of supersaturation.

Nucleation has been shown to be a critical event during the EFC process (Rousseau and Sharpe 1980; Louhi-Kultanen 1996; Vaessen *et al.* 2003b; Petzold and Aguilera 2009; Peters *et al.* 2016; Quist-Jensen *et al.* 2017). The nucleation step has been found to depend on the degree of supersaturation and surface tensions between solid and liquid phases (Mullin 2001; Mersmann *et al.* 2002). There is always a competition between nucleation and growth. This process tends to transform a big number of small crystals into a smaller number of larger crystals. Vaessen *et al.* (2003b) observed the onset of nucleation during EFC, in a batch system, as a sudden presence of crystals throughout the crystallizer, with a simultaneous abrupt increase in temperature. According to Quist-Jensen *et al.* (2017), one of the keys to achieving favorable results with EFC is by establishing steady, relatively uniform conditions of nucleation and growth. In principle, the nucleation can occur either at a chilled surface, on the surface of seed crystals (see later), on impurities or particles that happen to be present within the mixture, or at the interface of droplets of chilled fluids that are being used for direct EFC systems.

Principles underlying the EFC process, as described in the literature (Barduhn and Manudhane 1979; Avram *et al.* 2004; Lewis *et al.* 2010; Becheleni *et al.* 2017), can be understood from the phase diagram in Fig. 1 (see Stepakoff *et al.* 1974). As shown, the phase equilibrium depends on both the temperature and the solute concentration. For solutions with concentration lower than the eutectic concentration, referred to as hypoeutectic solutions, sufficient cooling results in the crystallization of ice, which will co-exist with the solution. As more ice is removed, the solution becomes more concentrated, resulting in an increased freezing point depression. Thereby, the system tends towards the eutectic point, shown by the red dot. At this point, further cooling will cause simultaneous crystallization of both ice and salt. If the solute concentration is higher than the eutectic concentration, referred to as hypereutectic solutions, cooling will result in crystallization of salt, which reduces the solution concentration. Likewise, as more salt is removed, the system tends towards the eutectic point. When the process is carried out batchwise, the temperature of the system initially may be chilled to below the eutectic point, but upon nucleation of crystals, the temperature quickly rises and stabilizes near the eutectic point due to the release of heat of fusion (Himawan *et al.* 2006).

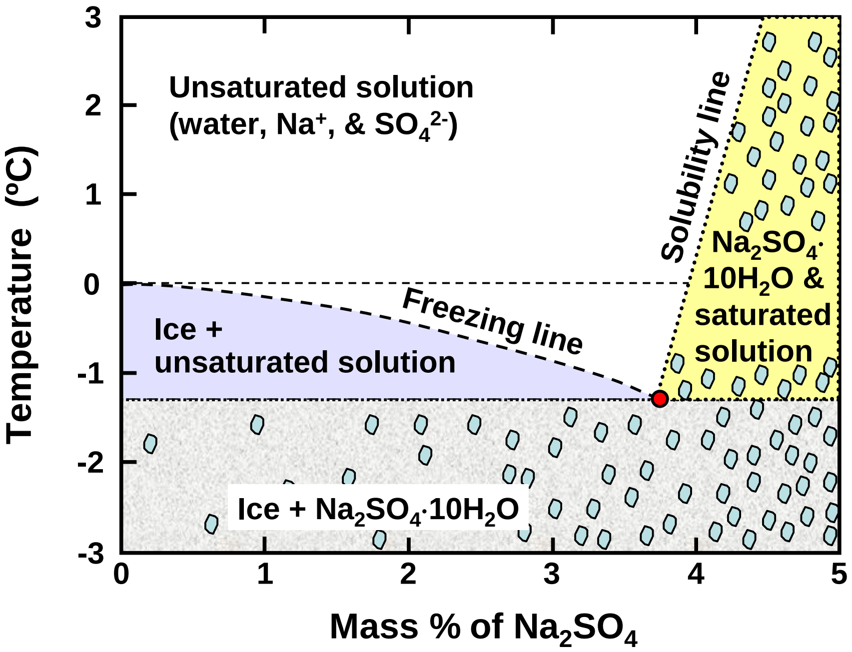

Fig. 1. Schematic diagram illustrating the phase behavior of mixtures of sodium sulfate and water, depending on concentration and temperature. The red circle corresponds to the eutectic point, as determined by Pronk (2007).

Under laboratory conditions it is possible to obtain salt crystals that are relatively free of other materials (Rodriguez-Pascual 2010). Hasan and Louhi-Kultanen (2016) determined that water obtained by the freeze crystallization process as ice contained only 38 ppm of nickel sulfate. Vaessen *et al.* (2003a,b) reported that the level of solute contamination (KNO_3-HNO_3) within ice from EFC was less than 5 ppm or 15 ppm in different cases. On the other hand, if high purity of the produced ice is not needed, then a higher level of supersaturation can be employed; such adjustments can allow for faster processing (van der Ham *et al.* 2004).

In principle, as the rate of growth of ice increases, it can become increasingly challenging to avoid entrapment of solute within the ice crystals. Especially in the absence of stirring, a concentration gradient will develop ahead of the advancing front of freezing ice (Burton *et al.* 1953; Terwilliger and Dizio 1970). In such circumstances, a high concentration of solute in the immediate neighborhood of the interface increases the likelihood of engulfment, as ice surrounds pockets of solution (Gerbasi *et al.* 1993). In addition, when the chilled crystallizer surface is sufficiently colder than the equilibrium freezing point of the adjacent aqueous solution, dendritic ice can form, and the growth rate of such ice can be two orders of magnitude higher than the rate of growth of a perfectly flat interface (Kapembwa *et al.* 2013). Butler (2002) reported the contamination of ice in a direct cooling EFC system with a certain type of antifreeze. In that case the ice contamination was attributed not only to a rapid advancing of the interface, but also to a crystalline similarity between the ice and the molecular structure of the solute. Also, relatively large molecules, having low rates of diffusion, will have a greater tendency to contaminate a growing crystal of ice in the absence of stirring.

Even in mixtures containing more than one solvent, various researchers have documented the recovery of relatively pure inorganic compounds from EFC processes. For instance, Rodriguez-Pascual *et al.* (2010) managed to separate pure ice and pure sodium carbonate from an industrial process sample. Vaessen *et al.* (2003a,b) isolated very pure potassium nitrate from a eutectic solution that also contained nitric acid.

Indirect Cooling EFC

Since there have been many publications dealing with so-called “indirect cooling eutectic freeze crystallization,” that type of system will be considered here first. The word “indirect” means that the system is cooled at a metal surface by circulating a coolant on the other side of the metal (Vaessen *et al.* 2002; Rodriguez-Pascual *et al.* 2010; Van Spronsen *et al.* 2010; Hasan *et al.* 2017a). An inherent advantage of such methods is that no coolant ever comes into contact with the processed materials, thus minimizing the chance of contamination. On the other hand, an indirect EFC system can suffer from problems related to build-up of ice layers and other scale on the chilled surfaces, in addition to ice and salt separation challenges, as described next.

Scale formation

Several authors have called attention to a problem of markedly reduced heat transfer following the development of a layer of ice on a cooled surface (Vaessen *et al.* 2002; Pronk *et al.* 2008; Hasan *et al.* 2017a). According to Hasan *et al.* 2017a), the formation of an ice layer is perhaps one of the key issues standing in the way of implementation of EFC technology at an industrial scale.

The rate of ice growth on a chilled surface can be complex, often involving a delay period before ice growth begins to interfere with EFC operations (Vaessen *et al.* 2003a). Vaessen *et al.* (2003a) noted that it can take several hours for ice to grow to a detectable level on a cooled wall of an EFC device. Hasan *et al.* (2017a) observed a time delay, before ice formation, that depended on both the temperature depression below the eutectic point and the rate of agitation. Delay times in the range of about 5 minutes to over an hour were observed. Engineers often have based their estimates of ice build-up on a square-root-of-time growth rate (Ashton 1989). For instance, Hasan and Louhi-Kultanen (2015) observed that the advancement of the thermal and concentration boundary layer at the ice-solution interface was proportional to the square-root of freezing time. However, based on inspection of data from several studies, the cited authors showed that the initial rate of ice growth is generally linear with time, and then there is a transition to a $t^{0.5}$ dependency. As will be described later, the temperature plays a key role with respect to the onset of ice accumulation. The dynamics of ice growth during EFC has been predicted by simulation (Himawan *et al.* 2002; Lotfollahi 2009).

Scraping

Several studies have been carried out to evaluate parameters related to the scraping of chilled surfaces during indirect EFC (Vaessen *et al.* 2002, 2003a,b; Roos *et al.* 2003; Genceli *et al.* 2005; Rodriguez-Pascual *et al.* 2010; Van Spronsen *et al.* 2010; Hasan *et al.*

2017a). For example, Vaessen *et al.* (2002) observed that either PTFE or silicon scrapers were effective in removing ice crystals from a chilled surface. The effect could not be attributed to mere refreshing of the surface due to flow. In the absence of using mechanical force, the ice built up after its nucleation.

Jooste (2016) investigated the effects of heat transfer driving force, scraper speed, solute type, and concentration of inorganic impurities on the induction time of ice scale formation, with longer induction times being favorable for the operation of an EFC process. An increase in heat transfer driving force resulted in a decrease in induction time due to the higher supersaturation generated at the wall, while an increase in scraper speed, solute concentration, and concentration of impurities resulted in an increase in the induction time of scale formation. From this, it can be generally inferred that real solutions will have lower scaling potential than pure binary systems due to the presence of contaminants in the system.

Little attention appears to have been devoted to smoothness or roughness of the chilled surface in the case of EFC. Hirata *et al.* (2000) studied the formation and removal of ice crystals on a chilled polyvinyl chloride (PVC) plate. Ice crystals that formed on the as-received PVC surface readily detached themselves. However, ice that formed on a PVC surface that had been sanded did not spontaneously separate from the PVC.

Separation by density

In principle, the ice particles and crystals of inorganic compounds formed during an EFC process can be separated by gravity. Such a separation can happen if both types of crystals are free from any chilled surfaces so that they are individually suspended in the saturated solution. For example, Rodriguez-Pascual *et al.* (2010) reported that only small amounts of sodium carbonate were dragged upwards with the rising ice particles and essentially no ice was dragged downwards with the settling sodium carbonate. Typical eutectic solutions of inorganic compounds have densities in the range of 1.1 to 1.2 g/cm^3 (Chen *et al.* 1980; Vaessen *et al.* 2003b). Water ice, by contrast, has a density of 0.90 g/cm^3 (Vaessen *et al.* 2003b), and various salt crystals have higher densities (Vaessen *et al.* 2003b). Specifically, the density of sodium sulfate, in its common decahydrate form (Thompson and Nelson 1954; Toghiani *et al.* 2008; Fernández-Torres *et al.* 2013), is about 1.464 g/cm^3 (Becheleni *et al.* 2017).

Another key factor that affects separation by gravity is particle size. Studies of the EFC process have reported ice particle sizes in the range 50 to 200 μm (Vaessen *et al.* 2003b; Reddy *et al.* 2010; Cob *et al.* 2014). Becheleni *et al.* (2017) observed ice crystals as large as 1 mm. However, it is clear that the ice particle size can be a function of such factors as the supersaturation at nucleation and the residence time (Chivavava *et al.* 2014). Increase in supercooling yielded larger ice particles. Himawan *et al.* (2002), in their simulation study, predicted sizes of ice particles in the range of about 50 to 500 μm. The same authors predicted sizes of NaCl particles in the range of about 100 to 140 μm. Reddy *et al.* (2010) and Peters *et al.* (2016) reported sodium sulfate decahydrate particles in the range of 20 to 400 μm and 32 to 171 μm, respectively.

If one assumes sphere-like particles having a diameter of 100 μm, then the cited density values imply rates of ice floatation and Na_2SO_4 settling of about 6 cm/min and 12 cm/min, respectively, based on the Stokes equation (Batchelor 1967) and the viscosity of cold water,

$$v = \frac{2}{9}\frac{(\rho_p - \rho_f)}{\mu} g R^2 \qquad (1)$$

where v is the terminal velocity, ρ_p is the density of the particle, ρ_f is the density of the fluid, μ is the shear viscosity of the fluid, g is the acceleration of gravity, and R is the particle radius. It is important to note that EFC may involve turbulent flow, due to the action of scrapers. Since the Stokes equation does not take such flows into account, the equation, taken alone, can predict only the net movements of particles relative to the local fluid surrounding them.

Because EFC can involve relatively high concentrations of particles in suspension, there can be deviations from the Stokes equation. Richardson and Zaki (1954) considered such systems in the case of uniform spheres. The equation that they derived can be regarded as a version the Stokes equation that contains a correction term. The correction was found to become significant for volumetric concentrations above about 5%.

The effectiveness of separation can also be affected by the morphology of the crystals, which depends on factors such as the degree of supersaturation and presence of impurities in the system. As discussed earlier, dendritic ice forms at high supercooling levels and tends to attach to crystallizer surfaces and also encapsulate some salt crystals, implying that the floating rate is impeded. Certain salts have been observed to crystallize in different shapes than their thermodynamically predicted shapes in the presence of impurities, which affects the settling rates of such particles (Buchfink 2011). Not only does morphology affect separation, but also it has an influence on the efficiency of downstream processes, such as washing and drying.

Hydrocyclones are known to be effective for separation of both light and heavy particles from suspensions (Rietema 1961; Narashimha *et al.* 2007). As reported by Stepakoff *et al.* (1974), hydrocyclones can be employed for effective separation of ice (which emerges from the large end of the hydrocyclone) and salt (which emerges from the small end of the hydrocyclone). The advantage of such a system is that the driving force for separation is greatly increased relative to ordinary gravitational acceleration. So although much of the ice and inorganic compound can be expected to separate themselves by gravity alone, there is potential to use hydrocyclones to divide the remaining mixture into one fraction that contains only salt (together with solution) and another that contains only ice (together with the rest of the solution).

Certain designs of EFC devices have been claimed to facilitate the gravity separation of ice and inorganic compounds, though the reasons often are not completely known. According to Vaessen *et al.* (2003b), their design, involving a stack of cooled disks, each provided with scrapers, exhibited different zones of rising ice and settling salt crystals.

Washing

Although gravity can be used to achieve a gross separation of ice and inorganic compounds during an EFC process, washing stages may be used to remove impurities from both solid phases (Stepakoff *et al.* 1974; Vaessen *et al.* 2003a,b; Chivavava *et al.* 2014; Cob *et al.* 2014; Becheleni *et al.* 2017). Stepakoff *et al.* (1974) employed a column in which both floatation and washing of ice were achieved. Peters *et al.* (2016) reported that washing of an antiscalant from sodium sulfate and ice was highly effective, suggesting that any impurities were mainly physisorbed on the outsides of crystals. Becheleni *et al.* (2017) removed essentially 100% of sodium sulfate from ice by use of three stages of countercurrent washing with deionized water. However, it should be noted that optimal operational conditions in the EFC process have potential to enhance the washing efficiency. Contributions to better washing efficiency, by optimizing the EFC process, can include reduced incorporation of impurities into the solids and adjustments to achieve more effective separation of ice and salt. In other words, if the rising ice entrains large quantities of salt, then more washing is required to remove this salt from the ice with inevitable salt and ice losses.

Direct Cooling EFC

The words “direct cooling” imply that cooling is achieved by adding an insoluble refrigerant fluid to the system, which can then be recovered and recycled. The use of direct cooling in EFC systems was the subject of several studies (Stepakoff *et al.* 1974; Barduhn and Manudhane 1979; Chowdhury 1998; van der Ham *et al.* 1998). Chowdhury (1998) reported that butane, propane, and fluorocarbons, such as those used in refrigeration systems and air conditioners, can be suitable for use with EFC processes. Typically the refrigerant is injected into the system under pressure; upon absorption of heat energy, the refrigerant becomes vaporized and is recovered as a gas. As noted by van der Ham *et al.* (1998), direct cooling systems provide a way to avoid ice scaling. No more recent reports of direct cooling EFC systems were found in the present search of the literature.

FACTORS AFFECTING PERFORMANCE OF EFC

Having considered, in the previous section, the principles of operation of EFC processes, the focus in this section will be on what has been published about tailoring or optimizing the process, with a focus on the type of separation that could be useful for recovering sodium sulfate, and possibly other solids, from spent pulping liquor.

Temperature Difference from Eutectic Point

Many studies have emphasized the importance of operating at low supercooling levels, that is, the temperature deviation from the eutectic temperature. Attention to the temperature of the coolant, so that the chilled surface is not excessively cooled, can prevent or at least reduce scale formation in an EFC process (Barduhn and Manudhane (1979; Vaessen *et al.* 2003a,b; van Spronsen *et al.* 2010; Chivavava *et al.* 2014; Kapembwa *et al.* 2014). Stepakoff *et al.* (1974) used a coolant temperature of -21 °C for EFC processing of water containing NaCl, matching the eutectic point. Barduhn and Manudhane (1979) recommended that the coolant temperature of an EFC natural water system (Na, K, Ca, Mg, Cl, SO_4, HCO_3) be no lower than –25 °C. According to these sources, depending on the eutectic point of the mixture, it is possible to choose a coolant temperature that is low enough to favor crystallization but not so low as to promote excessive scale formation on the chilled surfaces. Generally, low supersaturation favors steady crystal growth over nucleation, whereas high supersaturation results in domination of nucleation over growth, resulting in fine crystals and an impure product (Mullin 2001; Myerson 2002; Lewis *et al.* 2015).

Scraping Rate and Agitation

Some studies have varied the frequency with which chilled surfaces are scraped (Vaessen *et al.* 2002, 2003b). According to Vaessen *et al.* (2002) the way that scrapers impede the development of scale is by continually removing the initial crystals from which a contiguous layer of scale would continue to grow. The cited authors also found that the required rate of scraping tended to increase with increasing levels of supersaturation (decreasing surface temperatures) in the EFC system. An optimum scraping rate appeared to aid in the gravitational separation of the ice and salt crystals, with the development of separate zones for floating and settling (Vaessen *et al.* 2003b).

Some evidence suggests that at least part of the benefit of scraping action may be in reducing the boundary layer of stagnant fluid that tends to limit heat transfer at wetted surfaces. For instance, Vaessen *et al.* (2003b) stated that the fact that the heat transfer coefficient increased as the square-root of the scraping rate was consistent with the removal of a boundary layer (*i.e.* the penetration theory). The scraper action was reported to aid in convection (Vaessen *et al.* 2003a). Jooste (2016) also observed that increase in scraper speed delayed the onset of scale formation at constant heat transfer driving force. Direct agitation also can provide benefits. It was reported by van der Ham *et al.* (2004) that agitator use can minimize scale formation. Ahmad *et al.* (2017) reported benefits of agitator use in an EFC system; mechanical stirring, ultrasonic vibrations, and bubbling all were beneficial. Hasan *et al.* (2017a) noted that a higher intensity of agitation or a lower degree of cooling below the eutectic point both tended to delay the onset of scale formation on the chilled surfaces. When pushing the temperature of the chilled surface to relatively low levels, the benefits of agitation became pronounced. The heat transfer was increased.

Design of the EFC Unit

At the laboratory or pilot equipment scale, researchers have tested several design concepts in an attempt to make the EFC process work more effectively, focusing on indirect cooling by means of chilled surfaces. Table 1 categorizes such studies in terms of some essential design elements. Figure 2 (parts a, b, and c) provides some schematic sketches to show the essential geometries of the respective systems. The design used by Rodriguez-Pascual *et al.* (2010) incorporated an inverted cone at the top of the chilling chamber; this device cause the floating ice to drift to the edges of the chamber, where it could overflow and be collected.

Table 1. Design Concepts for EFC Equipment

Design Concept	Attributes	Literature Citations
Disc column	Rotating scrapers	van der Ham *et al.* 1998, 2004; Genceli *et al.* 2005
Inner & outer wall of annular vessel	Rotating scrapers	Vaessen *et al.* 2003
Cylindrical chilling modules	Rotating scrapers	Rodriguez-Pascual *et al.* 2010

A key theme that is common to the research work represented in Table 1 is that the scraping operation can be vital to effective performance of an EFC unit. Functions of the scrapers can include (a) repeatedly dislodging any crystals of ice or inorganic compounds from the chilled surface, which will favor further crystal growth in the bulk, rather than on the chilled surface; (b) physically encouraging the solids to move away from the chilled surfaces, such that separation according to density can take place; and (c) increasing of the thermal conductance near the interface of the highly conductive metal and the relatively low thermal conductance of a stagnant layer of aqueous solution (Himawan and Witkamp 2002; Vaessen *et al.* 2003a).

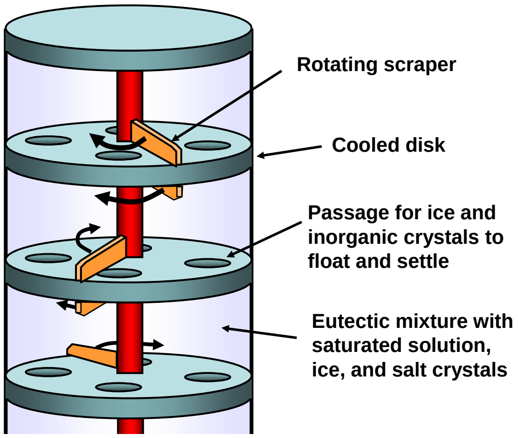

Fig. 2A. Schematic illustration of a cooled disk crystallizing unit for eutectic freeze crystallization, as described by van der Ham *et al.* (2004)

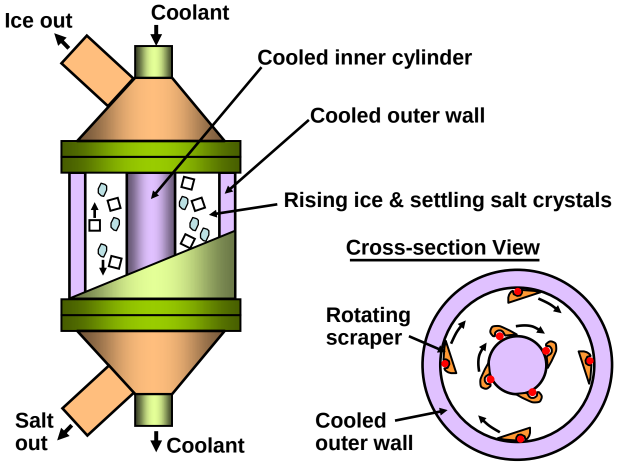

Fig. 2B. Schematic illustration of a cylindrical chilling module crystallizing unit for eutectic freeze crystallization, as described by Vaessen *et al.* (2003)

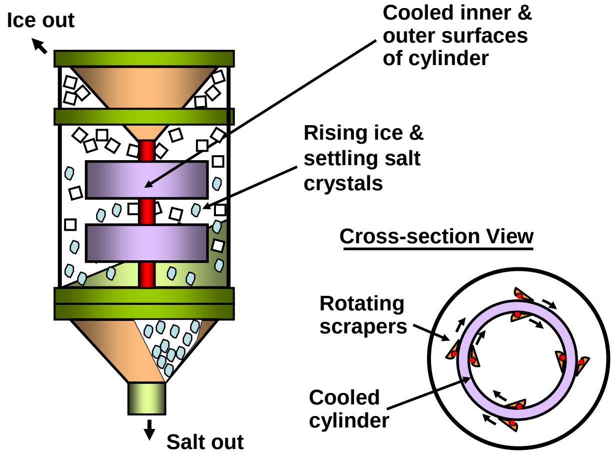

Fig. 2C. Schematic illustration of a concentric cylinders crystallizing unit for eutectic freeze crystallization, as described by Rodriguez-Pascual *et al.* (2010)

The orientation of the chilled surface is different in certain designs. The disc-type system pioneered by van der Ham *et al.* (1998, 2004) presents mainly horizontal chilled surfaces. From a practical standpoint, such a geometry would appear to be rather complex, providing possibilities for particles to either float or settle into positions where they could get stuck. By contrast, the designs that are here called "inner & outer wall of annular vessel" and "cylindrical chilling modules" present vertical walls, from which ice or inorganic compounds would be able to rise or fall without running into any obstructions. However, it would appear that there is an opportunity for further simplification of design, by incorporating the chilled surface as the outer wall of a cylindrical vessel, as illustrated in Fig. 3. Such simplicity would be obtained at the penalty for a lower area of chilled surface, in comparison to the system shown in Fig. 2B.

The reason that Fig. 3 depicts ice mainly rising in the central part of the crystallization unit is due to the mild centrifugal effect imparted by the rotating scrapers. Depending on the rate of rotation, it is likely that the centrifugal effect will be enough to impart a preference for sodium sulfate to settle near to the outside perimeter of the crystallization unit and for the ice to tend to channel upwards near the axis of the unit. A minor spray of water, from the top of the unit, can serve as a first step in removing inorganics from the ice particle surfaces.

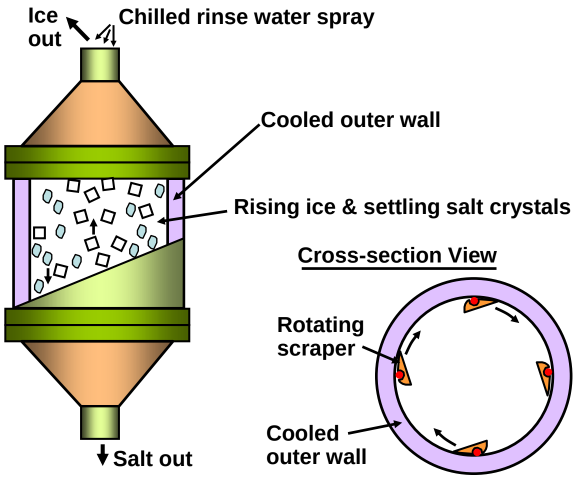

Fig. 3. Simplified crystallizing unit for eutectic freeze crystallization

Avram *et al.* (2004) describe the innovation of tilting the orientation of an EFC device. Such a strategy was found to encourage the flow of ice upwards on one side of the device and downward flow of the crystals on the other side. Such convection was said to allow continuous operation at the laboratory scale.

Regarding the scraper, it is clear from the literature that researchers have been concerned not only about the durability of the scraper, but also the need to avoid damaging the chilled surface. Vaessen *et al.* (2003b) as well as Rodriguez-Pascual *et al.* (2010) employed high density polyethylene (HDPE) scraper blades, which appeared to be durable enough for their lab-scale work. In the publication of van der Ham and co-authors (1998, 2004), though no details of the scraper design are provided, the word "wipe" is used to describe their function, suggesting that the action could be described as gentle.

STRATEGIES FOR APPLYING EFC TECHNOLOGY TO BLACK LIQUOR

Overview

One of the great challenges of applying a technology such as EFC to the recovery of pulping chemicals from spent pulping liquor is that the systems are highly impure, containing a wide range of both organic and inorganic compounds. While it is likely possible to nucleate ice crystals within as-received pulping liquor, the tar-like character, due to the presence and enrichment of lignin and other organic compounds, can be expected to impede the separation of the ice and other newly formed crystalline materials, such as sodium sulfate.

Crude black liquor, immediately after it has been removed from the fibers in the brown-stock washers, typically has a solids content of about 15% (Tikka 2008; Kousini *et al.* 2016). According to Bajpai (2017), organic compounds typically comprise about 2/3 of the dissolved solids content of black liquor, and the other 1/3 are inorganic compounds. As noted by Empie (2009), the main inorganic components are sodium hydroxide, sodium sulfate, sodium carbonate, and any unreacted sodium sulfide. According to Kevlich *et al.* (2017), most of the reduced sulfur is likely to be present in black liquor as thiosulfate, *e.g.* $Na_2S_2O_3$. Other inorganic components can include sodium chloride and various compounds related to silica.

Table 2 summarizes the types and amounts of inorganic compounds typically present in black liquor (Clayton *et al.* 1989; Niemelä and Alén 1999). The second and third numerical rows in the table provide estimates of the corresponding amounts of compounds following a hypothetical oxidation step (converting any reduced sulfur species to sulfate), or a combination of oxidation and neutralization of the pH. In addition, black liquor will contain poly-aromatic lignin byproducts, saccharidic compounds (mainly from the hemicelluloses), low mass organic acids, and extractives, which will include fatty acids and resin acids. The pH of typical black liquor is in the range 11.5 to 12.5. Bajpai (2017) notes that most of the carbohydrates solubilized in black liquor are monomeric, whereas lignin breakdown products have a wide range of molecular mass. It is also possible that a black liquor sample could contain NaCl (Kevlich *et al.* 2017); this is undesirable due to the corrosive nature of chloride toward stainless steel. Due to the high solubility of NaCl, it will tend to be among the last compounds to precipitate during EFC processing.

Table 2. Inorganic Composition of Typical Black Liquor (wt.% based on initial)

Inorganic compound:	Na_2SO_4	Na_2CO_3	$Na_2S_2O_3$	Na_2SO_3	Na_2S	NaOH	SiO_2 and related
Composition as reported *	10 to 15	35 to 40	15 to 20	5 to 10	15 to 20	5 to 10	0.2 to 0.7; 1 to 30 **
Composition after oxidation	70 to 99	35 to 40	0	0	0	0 to 3	0.2 to 0.7; 1 to 30 **
Comp. after neutralization	10 to 15	42 to 53	15 to 20	5 to 10	15 to 20	0	0.2 to 0.7; 1 to 30 **
Comp. after oxidation and neutralization	70 to 99	35 to 44	0	0	0	0	0.2 to 0.7; 1 to 30 **

* data from Clayton *et al.* 1989 and Niemelä and Alén 1999; ** The higher number range for SiO_2 pertains to grasses (Kevlich *et al.* 2017). See the Appendix regarding the assumed stoichiometry used to determine the values in the last two rows.

Lignin Removal

Though the topic of lignin removal from black liquor will be reviewed in more detail in a later article, some key aspects will be summarized here. It is well known that though lignin byproducts tend to be soluble at the very high pH values of spent pulping liquors, the solubility is markedly decreased when the pH is lowered. The reason to consider removing lignin by acidification, prior to the EFC process, is that it might precipitate out during EFC processing, thus contaminating the equipment. If it does not precipitate, it would get concentrated, thus raising the solution viscosity, hindering effective separation of ice and salt, and possibly contaminating the final products. Spent pulping liquor is known to become quite viscous as water is removed (Empie 2009), and the cold temperatures associated with EFC can be expected to favor a tar-like or solid-like character of the organic content of black liquor. Tikka (2008) lists marked increases in black liquor viscosity with decreasing temperature even when the lowest temperature considered was 90 °C.

It has been well demonstrated that the majority of the lignin-related compounds in kraft liquor can be separated and recovered when the pH of the spent liquor is suitably reduced (Alén *et al.* 1979; Loutfi *et al.* 1991; Gilarranz *et al.* 1998; Stoklosa *et al.* 2013; Dominguez-Robles *et al.* 2016; Kousini *et al.* 2016). In particular, carbon dioxide, which is readily available from combustion processes at pulp and paper mills, can be used to reduce the pH to near-neutral or moderately acidic values, thus bringing about the precipitation of lignin (Alén *et al.* 1979; Wienhaus *et al.* 1990; Loutfi *et al.* 1991; Wallmo *et al.* 2009; Kousini *et al.* 2016). The use of carbon dioxide in this process presents great economic benefits due to its in-house availability. Under the hot conditions typically employed in such processing, the lignin phase can be separated and recovered as a water-insoluble liquid (Stoklosa *et al.* 2013).

Alternatively, the following cited studies represent considerable research work that has been carried out to concentrate lignin by ultrafiltration and related membrane methods (Holmqvist *et al.* 2005; Giummarella *et al.* 2016; Humpert *et al.* 2016; Kevlich *et al.* 2017). Relative to the just-described acidification and precipitation work, the use of membrane separation seems to have some important disadvantages. One of them is that the concentrated lignin remains in solution form; thus it is not truly isolated. The other problem is that other substances in the concentrate can include extractable materials (fatty acids, resin acids, unsaponifiable materials, *etc.*), as well as hemicellulose breakdown products. It is unclear whether such a mixture would have commercial value without further steps to isolate the components.

Optional Isolation of Extractives from Spent Pulping Liquor

In a conventional chemical recovery operation, in the course of evaporating the spent pulping liquor there is opportunity to separate out some of the relatively hydrophobic components that become released from the lignocellulosic material during pulping. The extractive fraction, which is collectively called “soap,” often comprises 30 to 50 kg per ton of black liquor solids (Foran 1992). This will include fatty acids, resin acids, and unsaponifiable materials (Pirttinen *et al.* 2007; Laxén and Tikka 2008). In a conventional recovery plant, such materials would be collectively called “tall oil” (Ren *et al.* 2016; Aro and Fatehi 2017). Typically, the separation is carried out after sufficient water has been evaporated from the black liquor to raise its dissolved solids content to about 20 to 30%; at that point the soap becomes insoluble and readily floats to the surface at near-boiling temperatures within a tank (Foran 1992; Aro and Fatehi 2017). According to Empie (2009) the lowest solubility of tall oil substances can be expected when the solids content is in the range of 25 to 28%. Crude soap skimmings will contain a wide range of components, including pulp fines and hemicellulose breakdown products (Ren *et al.* 2016).

Some of the extractive materials are likely to be precipitated along with the lignin, if the facility were to implement an acidification process (Stoklosa *et al.* 2013). According to Laxén and Tikka (2008), acidification of black liquor either with carbon dioxide or with other acids will tend to bring about precipitation of the fatty acids and resin acids. Any unsaponifiable compounds (neutrals) that have been emulsified by the soap compounds would then precipitate as well. Laxén and Tikka (2008) suggested that full separation of the tall oil fraction might require lowering the pH to a range of 2.6 to 3. However, as was noted earlier, there may be an opportunity to isolate a greater fraction of the extractives after an ultrafiltration operation before the black liquor pH is lowered; such treatment has the potential to retain most of the lignin, while allowing most extractives to pass through (Keyoumu *et al.* 2004; Manttari *et al.* 2015).

Foran (1992) noted that the separation of the extractive materials from black liquor can be promoted in various ways. If one depends only on gravity, then the equipment needs to be sized appropriately so that the slow creaming process can take place, making it possible to skim a floating layer of soap. Soap was reported as rising at a linear speed of about 1 to 6 meters per hour. Foran (1992) noted that the separation can be sped up by sparging the system with tiny air bubbles, leading to floatation of the hydrophobic droplets. In principle, one also could consider the use of hydrocyclones to speed up the density-dependent separation (Rietma 1961; Narasimha *et al.* 2007).

Already in 1998, McGinnis *et al.* had established that such separation of extractives could be enhanced by addition of surfactants. Pirttinen *et al.* (2007) showed that such a separation could also include neutral soluble species. Thus, the sterols, alkanols, and aliphatic compounds present in the pulping liquor will tend to be removed along with the more surface-active resin acids and fatty acids. Ren *et al.* (2016) were able to separate not only extractives from black liquor, but also hemicellulose byproducts. Kenny *et al.* (1992) employed dissolved air floatation (DAF) to separate resinous materials from the concentrate prior to freeze crystallization to separate ice from the mixture.

Even if steps are undertaken to remove extractives prior to EFC, it is reasonable to expect some level of those materials to enter the EFC process. Tests under realistic conditions will be needed to answer questions about the levels and effects of such compounds and to determine optimum conditions of operation.

Pre-concentration by Reverse Osmosis

Although EFC requires less energy to increase the concentration of solids in comparison to evaporative technologies (Fritzmann *et al.* 2007; Khawaji *et al.* 2008; Burbano and Brankhuber 2012; Morillo *et al.* 2014), in some cases even greater savings can be expected when using a combination of reverse osmosis (RO) followed by EFC (Stepakoff *et al.* 1974; Elimelech and Phillip 2011). RO has become the most widely used technology for desalination throughout the world (Elimelech and Phillip 2011). The RO process uses pressure to force a combination of water and solutes toward a very exclusive semi-permeable membrane, and only the water is able to pass through (Lee *et al.* 2011). Such a process is called "reverse" osmosis because the differences in electrolyte concentration on the two sides of the membrane ordinarily would induce flow in the opposite direction, *i.e.* a process of osmosis. One of the advantages of RO is that the process, if successfully implemented, can achieve highly pure water, having low ionic strength, and such water can have many uses within an industrial facility.

Past studies have shown that RO systems can be cost-effective for separation of relatively pure water from solutions that contain low to moderate concentrations of dissolved substances (Burbano and Brankhuber 2012). Various strategies to maximize the upper practical level of brine concentration that can be applied to an RO system have been discussed elsewhere (Burbano and Brankhuber 2012; Subramani and Jacangelo 2014). Eventually, however, one reaches a point at which the resulting brine is concentrated high enough to render further RO processing economically unattractive. The osmotic pressure that needs to be overcome to isolate additional fresh water approaches the capacity of the RO system. In addition, problems due to the fouling of RO membranes tend to become more severe at the limits of high pressure and high concentration of the brine. It has been estimated that RO can be used effectively to concentrate typical salts up to a concentration of about 7% (Tsai *et al.* 2017).

In the case of spent pulping liquor, even after most of the lignin has been removed by acidification and precipitation, the solution would most likely contain sodium sulfate, sodium carbonate, sodium thiosulfate, a variable amount of still-active sodium sulfide, hemicellulose decomposition products, wood extractives, and other inorganic ions including potassium, calcium, magnesium, manganese, iron, aluminum, oxalate, phosphate, chloride, and silicate ions (Venkatesh and Nguyen 1992; Engdahl *et al.* 2008; Empie 2009; Bajpai 2017).

EFC for Recovery of Selected Compounds

Sodium sulfate

Some of the major inorganic compounds that potentially can be precipitated from spent pulping liquor streams (possibly after removal of lignin, extractives, and some of the hemicellulose-related organics, as described above), include the sodium compounds sodium sulfate, sodium carbonate, sodium thiosulfate, sodium sulfite, sodium sulfide, sodium silicate, and sodium chloride.

Several authors have studied the eutectic freeze crystallization of sodium sulfate in the form of its hydrate with 10 parts of water (Thompson and Nelson 1954; Lewis *et al.* 2010; Reddy *et al.* 2010; Chivavava *et al.* 2014; Randall *et al.* 2014; Hasan *et al.* 2014; Hasan and Louhi-Kultnen; Hasan *et al.* 2017a,b; Becheleni *et al*. 2017). Some of the conditions of operations are shown in Table 3. As noted by Garrett (1998), the appearance and growth of crystals of sodium sulfate is a common occurrence in natural brine pools, especially when temperatures get cold in the winter. The ready formation of crystals of $NaSO_4 \cdot 10H_2O$ can be attributed partly to its lower solubility compared to other common salts such as sodium chloride. Thus, as shown in the table, the eutectic temperature for $NaSO_4 \cdot 10H_2O$ is only a little more than a degree below the freezing point of pure water.

The differences in the temperature at which sodium sulfate decahydrate was crystallized out can be attributed to different compositions of the starting solution. For a binary Na_2SO_4-H_2O system, the eutectic temperature at which both ice and $NaSO_4 \cdot 10H_2O$ crystallize out is in the range -1.1 to -1.2 °C. In the presence of impurities, the temperature can be different due to the effect of impurities on solubility and kinetics of the respective salt. It is known that the presence of common ions results in reduction of solubility, while some ions cause an opposite effect. The effect also depends on the concentration of impurities in the system. During the progress of a batchwise EFC operation, the temperature is expected to decrease when there is buildup of ions not participating in the crystal formation. For this reason, it is necessary to determine the relative nucleation temperatures of the salts from the spent pulping liquor to establish the energy requirements. This could be accomplished by thermodynamic modeling using software such as the OLI Stream Analyser and experimental verification.

Table 3. Conditions Employed for EFC Precipitation of Sodium Sulfate Decahydrate

Temperature (°C)	**Observations**	**Citation**
-8.2	Foundational work	Thompson & Nelson 1954
-1.2	Eutectic concentration = 3.8 wt.%	Pronk 2007
-1.3	Thermodynamic models; economic evaluation of EFC and evaporative crystallization.	Randall & Lewis 2009
+3.5	Theoretical prediction of temperature.	Lewis *et al.* 2010
-1.24	Crystallization initiated at -2.3 °C	Reddy *et al.* 2010
-1.1	Long residence time gave large crystals.	Chivavava *et al.* 2014
-3.9	Dye lowered the eutectic point.	Randall *et al.* 2014
-1.16	Phosphonate antiscalant had a moderate effect on crystallization kinetics of ice and salt.	Peters *et al.* 2016
-1.12 -1.17	Aqueous solution 4.1wt.% Phenol presence (0.2wt.%) improved growth rate and reduced nucleation rate.	Becheleni *et al*. 2017
-1.6 to -5.1	The focus was on the ice growth rate.	Hasan *et al.* 2017a

EFC isolation of more than one salt

Several authors have written about the ability to utilize successive stages of EFC to separately precipitate different inorganic compounds, each in relatively pure condition (Lewis *et al.* 2009; Afrasiabi and Shahbazali 2011). From the standpoint of pulping technology, the ability to remove non-participating chemical species from the process stream offers a great advantage; in conventional chemical recovery system, employing evaporation and a recovery boiler, substances such as potassium can act as a dead load on the process, lowering the overall efficiency (Engdahl *et al.* 2008; Bajpai 2017). Such materials can be partially purged from a conventional chemical recovery operation at a pulp mill only by their disposal as dregs from green liquor clarification (Cornell 1992). In the early work of Thompson and Nelson (1954), sodium sulfate decahydrate was precipitated at -8.2 °C, and this was followed by precipitation of sodium chloride at -22.8 °C. Nathoo *et al.* (2009) confirmed the cited results and added a thermodynamic analysis of systems for the sequential isolation of sodium sulfate decahydrate and sodium chloride by means of EFC. Randall *et al.* (2011) separated both calcium sulfate (98% pure) and sodium sulfate (96.4% pure) from brine. van Spronsen *et al.* (2010) reported the simultaneous precipitation of two compounds, sodium carbonate and sodium bicarbonate. The needle-like shapes of the bicarbonate salt filled up the voids in the crystal bed, resulting in poor filtration and low product purity. Neilly *et al.* (2009) discuss earlier work by Arakel and co-authors, who sequentially precipitated sodium sulfate, then sodium chloride.

One of the complications of multi-salt systems is that the combined eutectic point can be markedly depressed. For instance, Reddy *et al.* (2010) observed a eutectic point of -21.2 °C for Na_2SO_4 and water at high NaCl concentration, compared to a eutectic point of -1.24 °C for the pure binary system containing just sodium sulfate and water. In this case,

$Na_2SO_4.10H_2O$ crystallized first at about -10 °C followed by ice at -21.2 °C. If one wishes to crystallize Na_2SO_4 only, then the process will be maintained at the condition just before NaCl crystallizes, at the low temperature of -21 ºC.

In the case of the spent pulping liquor, the order in which salts are expected to crystallize out based on the eutectic temperatures of the binary salt-water systems published in literature is shown in Table 4. In each case, as a result of EFC processing, the concentrations of the ions associated with the material forming the crystals had risen to match the eutectic concentration. Table 4 shows the binary eutectic temperatures of the salts expected to crystallize. However, in the context of the spent pulping liquor, which is a multi-component solution, a thermodynamic model is required to determine the crystallization order of salts and their respective crystallization temperatures. In each case, as a result of EFC processing, the concentrations of the ions associated with a crystalline phase would have risen to its respective eutectic concentration. The presence of other salts and impurities can affect the nucleation temperatures of the salts.

Table 4. Anticipated Order of Crystallization of Salts Based on their Binary Eutectic Temperatures (van der Ham *et al.* 1999)

Salt	Binary eutectic temperature (°C)
$Na_2SO_4 \cdot 10H_2O$	-1.2
$Na_2CO_3.10H_2O$	-2.1
Na_2S, $Na_2S_2O_3$, silicates, *etc.*	-

There is need to verify these values by conducting a thermodynamic model of the actual system composition, since the presence of other salts and impurities can affect the nucleation temperatures of the salts (Lewis *et al.* 2009). NaOH has not been included here since it has a binary eutectic temperature of about -25 ºC and the economic viability of recovering NaOH could be unfavorable. Also, if the pH has been lowered by treatment with CO_2 to precipitate lignin, then the NaOH would already have been essentially converted to Na_2CO_3, as indicated in Table 2.

EFC precipitation of sodium carbonate

Garrett (1998) notes that sodium carbonate decahydrate (natron) is similar to mirabilite with respect to having a steep solubility curve, *i.e.* increasing the temperature does not rapidly increase its solubility. Thus it makes sense that natron can be the next main salt form to be precipitated in a sequential EFC process with a mixed brine. Rodriguez-Pascual *et al.* (2010) separated sodium carbonate and bicarbonate from aqueous solution by EFC. Coolant temperatures between -10 and -17.5 °C were employed, resulting in an operational temperature of -3.8 °C. The crystallizer was able to operate at a solids level as high as 36% by mass. Growth rates of ice were in the range 1 to 2×10^{-8} ms^{-1}, and those for sodium carbonate decahydrate were 3.5 to 8.3×10^{-9} ms^{-1}. van Spronson *et al.* (2010) extended the research at a larger scale and demonstrated a heat transfer rate of 5 $kW \cdot m^{-2}$. The preferred temperature of operation was -3.8 °C, which was just high enough to avoid co-precipitation of the sodium bicarbonate.

EFC precipitation of sodium chloride

Because of its relevance to desalination operations, there have been several studies focusing on the EFC precipitation of NaCl (Stepakoff *et al.* 1974; Cob *et al.* 2014; Hasan *et al.* 2014; Ahmad *et al.* 2017). Such a process is highly relevant to pulp and paper industry applications because the chloride ion is corrosive to stainless steels, and it could be helpful to remove such ions from the system. Table 5 shows the temperatures that have been used for EFC precipitation of NaCl. The economic feasibility of operating at such very low temperatures on an industrial scale needs to be assessed.

Table 5. Conditions Employed for EFC Precipitation of Sodium Chloride

Temperature (°C)	Observations	Citation
-21	Separation was achieved by direct cooling.	Stepakoff *et al.* 1974
-29.4	NaCl recovered in presence of other inorganics.	Cob *et al.* 2014

EFC precipitation of other inorganic compounds

Though sodium sulfate and sodium carbonate (as discussed above), are of particular relevance to the recovery of pulping chemicals, other compounds also have been isolated by EFC. These include calcium sulfate (Randall *et al.* 2011, 2013); magnesium sulfate (Genceli *et al.* 2005), nickel sulfate (Hasan and Louhi-Kultanen 2016), copper sulfate and mono-ammonium phosphate (van der Ham *et al.* 1999), sodium nitrate (van der Ham *et al.* 1998), and a mixture of potassium nitrate and nitric acid (Vaessen *et al.* 2003b).

Scale Management

Antiscalants

Because the chilled metal surface of an EFC precipitation cell is the coldest point accessible to the suspension, it follows that generally there is a high likelihood that either ice or the inorganic compound or both will tend to scale the surface. Peters *et al.* (2016) investigated the effect of a phosphonate-based anti-scale agent at different concentrations on the nucleation and growth rates of both ice and $Na_2SO_4 \cdot 10H_2O$ from a synthetic sodium sulfate solution. Both the ice and the salt precipitated during the EFC process exhibited measurable contamination by the antiscalant, though most of the antiscalant could be effectively washed off. Such washing would be attractive from the point of view of obtaining products of high purity. Generally, the nucleation rates of ice and salt were reduced in the bulk suspension. The study did not assess the effectiveness of the antiscalant in reducing scale formation on the crystallizer walls, but it can be generally inferred that antiscalants could reduce nucleation of scaling compounds on the chilled surface.

Ion exchange softening

A promising way to lower the likelihood or rate of problematic scale formation during EFC and related processes is to pre-emptively remove ions that have a propensity to form scale (Barduhn and Manudhani 1979; Subramani and Jacangelo 2014). Water softening, using ion exchange resins, is well known to be an effective way to remove Ca^{2+} and Mg^{2+}. Such ions, which contribute to water hardness, are associated with a variety of inorganic compounds that cause serious scaling problems in industry. Examples include calcium sulfate, calcium oxalate, calcium carbonate, and calcium phosphate (Gal *et al.* 1996; Severtson *et al.* 1999; Yu and Ni 2006; Du *et al.* 2009).

Scale formation also can be minimized in some cases by chemical compounds that react with problematic anionic species, for example by adsorption or precipitation. For instance, Burbano and Brankhuber (2012) reported that activated alumina can be used to remove silica from water, prior to EFC processing. Empie (2009) and Bajpai (2017) discuss several technologies that have been implemented in the recovery boiler system to remove silica; such approaches also could be considered as a pretreatment before EFC processing.

Temporary reheating

Temporary heating of the chilled surfaces of an EFC device has been shown to be an effective means of periodically eliminating any build-up of the main solids being precipitated (van der Ham *et al.* 2004). According to the cited authors, such heating can quickly release accumulated build-up, since the local conditions momentarily favor dissolution of both ice and the inorganic compound. Subsequently the EFC process can be started again with no apparent adverse consequences. Such a system could be optimized with adequate and effective process control to ensure that the instantaneous heating is not excessive, thereby disturbing the system's steady state. Kenny *et al.* (1992) likewise employed a "rapid heating" cycle to overcome problems related to ice buildup on chilled surfaces. The downside of such a strategy is that it will destabilize the crystallization operation. Every new cycle may need to be seeded, and a new steady state will need to be established.

Fluidized bed

By recirculating suitable insoluble particles within an EFC system, additional surfaces become available for potential nucleation of either ice or other inorganic compounds. Such an approach has been evaluated in the case of EFC (Pronk *et al.* 2006; Pronk 2007; Pronk *et al.* 2008). The cited work showed that the use of a fluidized bed approach was able to reduce the growth of an ice scale on the chilled wall during EFC. Steel balls were reported to remove crystals from the walls of the chilling device, and it was not necessary to utilize scrapers (Pronk *et al.* 2006). It also was reported that the fouling of the chilled walls was more severe under eutectic conditions, when both ice and salt were being formed, compared to when just one solid phase was being formed.

Seeding

In light of the concerns expressed in publications about scale formation in EFC systems, it makes sense to examine procedural steps that tend to avoid or minimize scale buildup. In principle, it is less likely for crystals of either ice or inorganic compounds to form on a chilled surface if there are numerous crystals of the same type already in suspension (Rousseau and Sharpe 1980). Thus, rather than nucleating on the chilled surface, the ice or other compound merely builds upon the surfaces of the respective crystals, increasing their size.

Several authors have reported the use of seeding as part of an EFC process (Stepakoff *et al.* 1974; van der Ham *et al.* 1999; Randall and Lewis 2009; Reddy *et al.* 2010; Peters *et al.* 2016; Becheleni *et al*. 2017). Chivavava *et al.* (2014) chilled a sodium sulfate solution to -2 °C and then induced nucleation of the supersaturated solution by adding crystals of ice. One can envision a system in which a part of the ice and inorganic crystals could be crushed and recycled as a means of greatly increasing the number and surface area of particles available for nucleation, without exceeding the optimum solids density beyond which the separation of ice and salt is interfered with.

Main Alternatives to EFC

While the main focus of the present article has been eutectic freeze crystallization (EFC), there are some related technologies that merit mention, if only to clarify how they differ from EFC. As noted by Subramani and Jacangelo (2014), there have been three main approaches used to minimize the volume of brines that result from reverse osmosis (RO) operations, and these are membrane-based, thermal based, and “emerging”. Of these three, the membrane-based approaches merely recover water and generate more concentrated brine, without any full resolution of the disposal problems associated with brines. Thermal approaches include, essentially, either evaporation or freezing as a means of separation of the phases. However, the two freezing-based approaches of EFC and membrane distillation are regarded by the cited authors as “emerging”.

Evaporative crystallization

In terms of capital equipment and the maturity of the technology, it may appear to be advantageous just to crystallize out salts by evaporation (Nathoo *et al.* 2009). However, in the cited work it was shown that, to achieve the same goals, EFC has the potential to reduce operating costs by between 80% and 85% relative to such a process. Further work will be needed to be able to make realistic estimates of energy savings. Attention needs to be paid to energy-saving methods, including multiple-effect evaporation. The cited authors also suggested that the relatively low capital cost of equipment for evaporative crystallization is consistent with its long period of scale-up and optimization within desalination plants around the world. Since EFC is an emerging technology, it is expected to undergo a similar scale-up and optimization cycle with significant cost reductions.

Membrane distillation and crystallization

The term “membrane distillation” refers to systems in which vacuum is applied to the accepts side of a membrane, allowing the liquid phase to evaporate and later be recondensed as a relatively pure liquid (Afrasiabi and Shahbazali 2011). According to Pérez-González *et al.* (2012), such operations are often carried out at 60 to 80 °C with an energy consumption of 15 to 20 kW h·m^{-3}. The equipment has a relatively small footprint, which can be important, especially when installing operations in an existing facility. Based on the cited accounts, it appears that most of the work related to membrane distillation has been focused on systems in which the main goal has been to obtain relatively pure water and where there is less interest in whether or not inorganic compounds can be obtained, especially in their pure form. Fouling is expected to be a key challenge to the successful implementation of membrane distillation systems (Afrasiabi and Shahbazali 2011). A design has been proposed recently for membrane distillation crystallization that takes into account the solubility curve of the crystallizing compound, so as to reduce fouling and energy consumption (Pantoja *et al.* 2015, 2016).

If membrane distillation is continued to the point at which the concentration of dissolved substances reach and begin to exceed their solubility, then there is potential to precipitate solids within the brine. Some recent publications have described such an approach in detail (Chen *et al.* 2014; Quist-Jensen *et al.* 2017). Because the process of evaporation generally causes the temperature of a system to decrease, it is conceivable that membrane distillation and crystallization carried out by application of vacuum might entail conditions that could match those of EFC systems. However, Pérez-González *et al.* (2012) state that membrane distillation operations are typically carried out at ambient pressure in the temperature range of 40 to 50 °C. Since the phase change involved in evaporation requires much more energy than the phase change involved with freezing, it seems unlikely that such membrane distillation methods will be able to approach the energy-efficiency of EFC. Another important difference is the dependency on use of a membrane, making the process susceptible to fouling. Future research, including scale-up efforts, will be needed in order to determine the relative seriousness of such challenges, especially in comparison to the challenges of scaling, throughput, and phase separation inherent in the EFC technology.

Curcio *et al.* (2010) describe an alternative approach in which membrane crystallization is combined with nanofiltration. Such as approach was evaluated for the removal of sodium sulfate from the effluent of a battery factory. A membrane crystallizer, positioned after the nanofiltration operation, produced the anhydrous form of sodium sulfate.

Anaerobic Treatment of Process Water

If some or all of the procedures already mentioned in this article were successfully combined together, bypassing usage of a furnace for the recovery of pulping chemicals and minimization of discharges to the environment, it is likely that there still would be an excessive level of contaminants in the liquid left over after removal of sodium sulfate, sodium carbonate, and possibly sodium sulfide, using a suitable number of stages of EFC processing. A major class of such contaminants is likely to be the organic breakdown products of hemicellulose. As has been reviewed recently (Hubbe *et al.* 2016), one of the most cost-effective ways to deal with such contaminated water is by use of an anaerobic reactor system. The up-flow anaerobic sludge blanket type of reactor is especially to be recommended, since it can readily convert hemicellulose-related organic compounds to methane, which is useful as a fuel. Since the bacteria responsible for anaerobic decomposition are often adversely affected by the inorganic components in the water (Isik 2004; Aslan and Sekerdag 2016), it is likely that the use of EFC to remove ionic compounds will have a positive effect on subsequent anaerobic digestion of the remaining material. Conditions of salinity may need to be optimized so that the combined system of EFC and anaerobic digestion works effectively. Although the contaminated water also could be treated using an aerated (aerobic) wastewater treatment system, such options tend to take up more space, produce more sludge, and there is no fuel byproduct. However, the details of potential upstream processing such as biological treatment techniques will not be dealt with in this article.

SCENARIOS FOR EFC IN PULPING OPERATIONS

Reactivation of the Pulping Chemicals

Return of sodium sulfate to a recovery boiler

A great advantage of conventional technology, employing a Tomlinson boiler for the recovery of pulping chemicals, is the fact that sodium sulfate can be converted to sodium sulfide in a reducing zone of the furnace (Cameron and Grace 1983, 1985). Such an option can be considered in a hypothetical case where EFC has been used to separate Na_2SO_4 and Na_2CO_3 from pulping liquor. For instance, there might be a pulp and paper mill in which EFC has been installed in order to overcome limitations in the capacity of an existing recovery boiler system. In such as case, the Na_2SO_4 from EFC could be fed with ordinary black liquor to the furnace. The relatively dry and pure condition of the Na_2SO_4 would tend to be favorable for such systems, since the heat load would be low and one could avoid the recycling of non-process elements such as potassium to the recovery cycle (Bajpai 2017). Trials would need to be carried out to achieve efficient and safe operation of a conventional chemical recovery boiler that incorporates the processing of extra Na_2SO_4 that is being isolated by EFC.

Separate conversion of sodium sulfate to sodium sulfide

One of the challenges inherent in replacing the conventional recovery process with something else is that changes will need to be made in how the sulfate becomes reduced to sulfide. In principle, reduction can be carried out at high temperature using different reducing agents, including hydrogen (Birk *et al.* 1971) and carbon monoxide (Li and van Heiningen 1988, 1995). The mechanism by which reduction takes place in the described systems can involve adsorption of sulfate at an interface. According to Cameron and Grace (1983, 1985), the mechanism of conventional recovery in a Tomlinson boiler involves adsorption of sulfate onto carbon within the hearth, where the reduction takes place. The reduced sulfur species then desorb. Li and van Heiningen (1988) found evidence of a similarly catalytic and surface-depending reaction (on a TiO_2 surface) when using CO as the reductant. Though the cited literature describes some procedures to carry out such reductions, it is unclear whether systems based on hydrogen or carbon monoxide would be cost-effective relative to conventional processing, in which carbon essentially acts as the reducing agent.

Electrolytic reduction of Na_2SO_4 and causticization of Na_2CO_3

The technologies just described, in which sulfate is reduced by adding carbon, CO, or hydrogen, all involve equilibrium reactions. By contrast, Wartena *et al.* (2000, 2002a,b) have investigated an electrolytic approach that can drive the reductive reaction essentially to completion. The process is carried out with a molten mixture of sodium sulfate and sodium carbonate, a combination that corresponds to what could be obtained using stages of EFC processing. In addition, any sodium carbonate present is simultaneously converted to sodium hydroxide, making it unnecessary to employ a lime kiln. Carbon dioxide is emitted as a byproduct. High conversion efficiency was observed at an operating temperature of 860 °C. According to Wartena *et al.* (2002a), a key to achieving success of this technology would be to provide a barrier between the cathode and anode, such that the reduced sulfur compounds are not re-oxidized by oxygen that is released from the other electrode.

Scale-up Considerations

As was noted earlier, recovery boiler systems tend to be large, and there has been no good way to increase the capacity of an existing boiler if a pulp mill wishes to expand its production. Some gains in production, using existing recovery systems, have been achieved by precipitating lignin from black liquor (Alén *et al.* 1979; Kousini *et al.* 2016). Though the reduction in burnable material being returned to the boiler is reduced, thereby decreasing the generation of energy, such strategies can permit a higher production of pulp at the facility.

A convenient aspect of EFC technology, at least as far as it has been developed to this point, is that the units are small – mainly scaled to lab and pilot-scale evaluations. Accordingly, one might consider pilot-scale trials in which EFC units are run along-side of an existing conventional chemical recovery operation. If such trials were successful, then the EFC unit could have potential to decrease the amount of evaporation needed in the recovery operation. More EFC units could be added incrementally, depending on the need for more chemical recovery capacity. A potential side-benefit of such a system is that the

EFC could function as a type of kidney, ideally returning only the valuable sodium sulfate, sodium carbonate, and possibly the reduced sulfur compounds to the cycle, while excluding such materials as potassium and manganese.

Concepts for a Combined Process

Preparative steps before EFC

Based on principles, materials, and unit operations discussed in earlier sections of this article, now it is possible to consider some possible scenarios by which EFC might be incorporated into a system to deal with black liquor. Figure 4 shows a possible sequence of steps that might precede EFC. In the envisioned process, the first step is an optional oxidation of the highly alkaline, hot black liquor. Such a treatment has been employed industrially as part of a lignin precipitation process in order to avoid later problems associated with reduced sulfur gases (Kouisni *et al.* 2016). The next step involves neutralization of the highly alkaline pH of the spent pulping liquor, thereby causing most of the lignin byproducts to precipitate from solution. Although such a step can be regarded as being unconventional, it has already been implemented in a few pulp mills as a means to achieve greater throughput of pulp production (Gellerstedt *et al.* 2013; Kouisni *et al.* 2016). Along with the lignin, some extractive materials can also be present in the precipitated material at this stage. The figure assumes that a system can be optimized to separately recover such extractives by a skimming process, while the greater density of the lignin phase would cause it to settle.

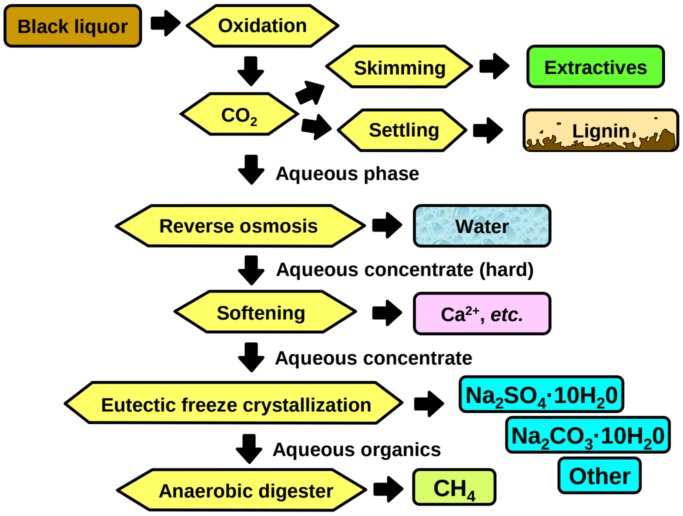

Fig. 4. Possible sequence of preparatory steps to remove components from spent pulping liquor in preparation for an EFC recovery of sodium sulfate and sodium carbonate

The next step shown in Fig. 4, reverse osmosis (RO), can be considered as a potentially cheaper way to separate relatively pure water from the aqueous mixture, depending on the concentrations of salts. It should be noted that RO operation may be subject to problems related to membrane fouling; relatively highly concentrated aqueous electrolytes and organic compounds can be expected to be in solution even after lignin removal. Evaluations could be carried out to optimize the target level of solids in the brine, before it is sent to EFC. On the other hand, if severe problems of membrane fouling are encountered with RO, there would be an option to omit the RO step in favor of complete reliance on freeze crystallization as a means of separation of water (as ice) from the other components of the mixture while concentrating it towards the eutectic conditions, at which point the operation becomes fully EFC.

The "softening" step listed in Fig. 4 implies usage of some sort of ion-exchange material. Higher-valence metal ions, especially Ca^{2+} and Mg^{2+}, would replace Na^+ ions on such resins. The objective of including such a step is to avoid problematic scaling of EFC equipment with such compounds as calcium carbonate, calcium oxalate, calcium sulfate, and calcium silicate. Such compounds also would have the potential to co-precipitate and contaminate the desired $Na_2SO_4 \cdot 10H_2O$ and $Na_2CO_3 \cdot 10H_2O$ during EFC operations. The topic of water softening has been well reviewed (Wachinski 2017).

After the EFC step (which will be discussed next), the last operation indicated in Fig. 4 is an anaerobic digester. The concentrated liquid phase left over after all of the EFC stages can be expected to contain a variety of water-soluble organic compounds. Such an aqueous mixture would be a good candidate for anaerobic digestion (Hubbe *et al.* 2016). The anaerobic digestion operation would generate methane, which can be used as a fuel or sold.

Multiple stages of EFC

Figure 5 envisions four potential stages of eutectic freeze crystallization. See Fig. 3 and the adjacent text for more detail regarding how such an EFC unit could incorporate scraping units and ice-washing operations. Due to the presence of other salts, it is not certain whether ice will precipitate when the temperature is cooled to near the eutectic point for $Na_2SO_4 \cdot 10H_2O$ in the presence of other ions. The diagram shows a process of crushing or grinding a small portion of the precipitated $Na_2SO_4 \cdot 10H_2O$ so that it can be immediately used as seed crystals, thus encouraging the formation of relatively pure $Na_2SO_4 \cdot 10H_2O$.

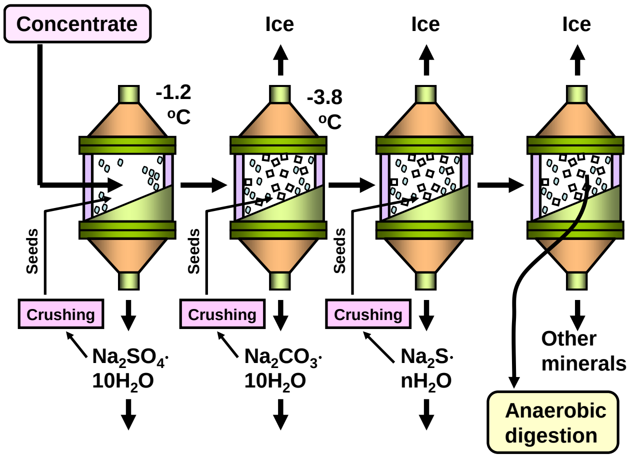

Fig. 5. Possible stages of eutectic freeze crystallization for continuous or batchwise separation of sodium sulfate decahydrate, sodium carbonate decahydrate, and possibly sodium sulfide from an aqueous concentrate (see previous figure)

Though Fig. 5 shows just four EFC units, it should be understood that the size and number of parallel units would need to be set according to the required production capacity and residence time in each unit. Though continuous operation is implied in the diagram, batchwise processing also can be considered. In a continuous operation, the liquid portion collected from the unit could pass to a subsequent unit, within which the temperature would tend to be lower, depending on the concentrations of ions present and the eutectic condition for the next compound to be collected.

The second EFC unit shown in Fig. 5 represents the precipitation of $Na_2CO_3 \cdot 10H_2O$. Though ice is shown in the figure as being generated from this unit, such ice precipitation would depend on the concentration of other electrolytes present. The feasibility of EFC to isolate $Na_2CO_3 \cdot 10H_2O$ is supported by previous work (Rodriguez-Pascual *et al.* 2010).

No account was found in the literature for the precipitation of sodium sulfide or sodium thiosulfate by EFC; thus the third unit shown in Fig. 5 can be regarded as speculative. Studies need to be carried out to determine whether or not Na_2S or Na_2SO_3, probably in a hydrated form, can be isolated by EFC. This is an important issue, since not all of the reduced forms of sulfur will have been consumed and converted to the sulfate form in a typical pulping cycle (Kevlich *et al.* 2017).

The final EFC unit depicted in Fig. 5 assumes that highly soluble inorganic compounds such as NaCl can be removed all together at a sufficiently low temperature, representing the eutectic point of the remaining mixture. This would allow the subsequent dry disposal and/or recovery and use of the precipitated salt mixture.

Reduction of the sodium sulfate and causticization of the sodium carbonate

Figure 6 depicts three main options (numbered 1, 2 and 3) for the conversion of sodium sulfate and sodium carbonate to the active forms (sodium sulfide and sodium hydroxide) required for pulping (*i.e.* white liquor). The options include (1) conventional processing in a recovery furnace, (2) separate reduction of the sodium sulfide, and (3) electroreduction. As stated earlier, if there is currently a recovery boiler in operation, then it makes sense to determine whether the additional sodium sulfate and sodium carbonate obtained from EFC can be just added into the black liquor fuel stream entering the boiler. The reduction of the sodium sulfate takes place within the reducing zone of the furnace, whereas the transfer of the alkalinity from sodium carbonate to sodium hydroxide (Cornell 1992) requires the use of a lime kiln (Venkatesh 1992) (see chemical process at the lower right within the figure).

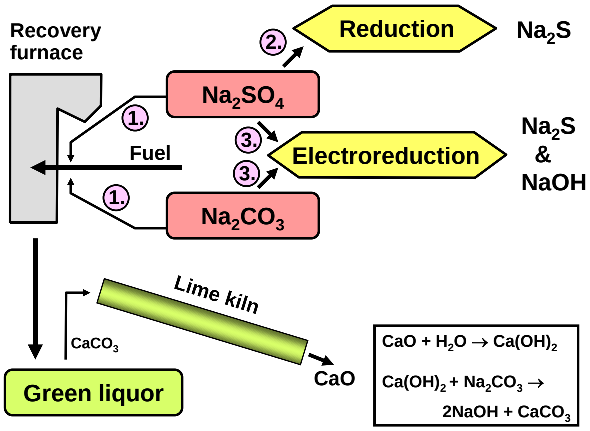

Fig. 6. Options for reduction of sodium sulfate and causticizing of sodium carbonate

If there is no recovery boiler system, or if such a system is not able to handle extra materials obtained by EFC, then a separate reduction of the sodium sulfate could be considered. Though, as discussed earlier in this article, it is possible to use hydrogen or carbon monoxide as reducing agents for such a step (Birk *et al.* 1971; Li and van Heiningen 1988, 1995), it seems likely that carbon would still be the most cost-effective reducing agent. This line of reasoning is consistent with the running of a separate furnace that might not be much different from a conventional recovery system, except that the input material (sodium sulfate, without lignin, carbohydrates, or other inorganic materials) could be much purer. It is uncertain what would be employed as the main fuel in such a system. Due to the lack of recent research dealing with the reduction of sodium sulfate in a carbon-based furnace system, it seems unlikely that such an approach would be commercialized in the foreseeable future.

The middle option of electroreduction shown on the right within Fig. 6 appears to be the most likely scenario in cases where a recovery boiler is not an option. As is apparent from the term “electroreduction,” the envisioned process involves the use of electricity to bring about the desired chemical transformation (Wartena *et al.* 2000). As noted earlier, the advantages include essentially complete conversion of the sodium sulfate and sodium carbonate to sodium sulfide and sodium hydroxide, respectively. Also, there is no opportunity for smelt-water explosions.

Incomplete conversion of sodium sulfate to sodium sulfide in a conventional recovery furnace renders such processes much less efficient. According to Empie (2009), about 5 to 10% of the sodium sulfate fails to be reduced in a typical recovery plant at a pulp mill. Such unconverted sodium sulfate goes through the subsequent cycle of pulping as a “dead load”. Likewise, in a typical lime kiln operation about 15 to 20% of the slaked lime ($Ca(OH)_2$) fails to be converted to NaOH. So along with such ionic materials as calcium, magnesium, iron, manganese, silicate, chloride, phosphate, and sulfate, the sodium sulfate and sodium carbonate will circulate in the reactivated (white) pulping liquor without making a contribution to pulping. Such considerations provide further incentive for researchers to run more evaluations of electroreduction (Wartena *et al.* 2000).

Whether or not electroreduction can ever achieve the cost-effectiveness of the conventional recovery systems used in the pulping industry, it might be ideal for relatively small-scale operations, filling a niche in cases where the construction of an economically viable recovery plant for spent pulping liquor cannot be justified.

CONCLUDING REMARKS

The scenario outlined in this review article explores an important area of potential innovation for the pulping industry. As noted in the Introduction, there is potential for reduced costs as well as for increased production rates, depending on how the described technology might be implemented in existing pulp mills. Some theoretical information, as well as some technological experiences have been documented here, hopefully providing a sense of how a system could be put together to achieve some of the many simultaneous objectives in a pulp mill that needs to process black liquor and regenerate pulping chemicals. Parts of the envisioned process have been demonstrated, though some of the demonstrations have been at a relatively small scale and with less complex starting mixtures compared to genuine black liquor. Thus, it can be expected that a lot of practical experimentation will be needed, involving a range of scientists and engineers, to move the technology forward toward industrial practice.

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APPENDIX

Assumed Stoichiometry for Calculated Values in Table 2

Formation of sodium sulfate (anhydrous basis)

Na_2S [78 g/mole] + $2O_2 \rightarrow Na_2SO_4$ [142 g/mole]

Ratio 142/78 = 1.82 (Na_2SO_4 formed per Na_2S oxidized)

Na_2SO_3 [126 g/mole] + ½ $O_2 \rightarrow Na_2SO_4$ [142 g/mole]

Ratio 142/126 = 1.13 (Na_2SO_4 formed per sulfite oxidized)

$Na_2S_2O_3$ [158 g/mole] + 2 O_2 + 2NaOH [40 x 2 = 80 g/2 moles] $\rightarrow$

2Na_2SO_4 [142 g/mole x 2 = 284 g/2 moles] + H_2O

$Ratio_1$ = 284/158 = 1.80 (Na_2SO_4 formed per thiosulfate oxidized)

$Ratio_2$ = 80/284 = 0.281 (NaOH used up per Na_2SO_4 formed)

Formation of sodium carbonate (anhydrous basis)

2 NaOH [2 x 40 g/mole = 80 g/mole] + $CO_2 \rightarrow Na_2CO_3$ [106 g/mole] + H_2O

Ratio = 106/80 = 1.32 (Na_2CO_3 formed per NaOH consumed)