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# Reject Brines from Desalination as Possible Sources for Environmental Technologies

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## 1. Introduction

Desalination of seawater represents the way to increase the supply of water for domestic, agricultural and industrial purposes. The potential environmental impact of desalination needs to be thoroughly evaluated, and any environmentally adverse consequences must be promptly addressed in order to assure a sustainable development of this technology.

The main concern in desalination is the management of the brines whose uncontrolled discharge has significant negative impacts on the environment. Indeed, even if the production costs have decreased in the last decade, those related to the disposal of the brine have shown only limited reduction of the relative costs. New production strategies benefit from modern and efficient freshwater-generation plants, but the management strategies are based only on the few traditional options for the disposal of wastes.

Sustainability is currently a main focus of high-level political discussions in the world, as it directly involves environmental pollution and global warming. Economic geologists are very well placed to understand and contribute to issues of sustainability, and to evaluate alternative resources for the future development of humanity. We, as economic geologists, are trained to unravel the complex series of events that led to the formation of natural resources. Consequently, we can use this expertise to help develop manmade processes to convert waste into resources.

Today, the challenge is to consider the brine, instead of a harmful by-product, as a valuable source for several compounds to be involved in diverse industrial processes. For example, the brines could provide significant amounts of magnesium, resulting in a very promising source of this element as an alternative to traditional mining. Indeed, today there are stringent regulations concerning mining in all most all countries to prevent or at least minimize damage to exploited properties. As traditional approaches in mining are costly in time or inapplicable in abandoned and remote regions, research needs to be focused on non-traditional sources such as brines coming from desalination plants. These brines certainly have several advantages, and in time can replace, at least in part, the conventional sources with an alternative, economically attractive process. Dual benefits can be achieved in recovering and recycling Mg from reject brines: reduction of large volumes of brines to be

discharged, as well as decrease of environmental concerns due to industrial extraction from silicate minerals.

In this chapter, we focus on novel processes making use of magnesium chloride of the reject brines as a reactant for the synthesis of minerals to convert the saline waste into useful and reusable solid products.

## 2. Background

### 2.1 The environmental concerns of reject brines

The increasing global population and industrial and agricultural production are driving a constant growth in the demand for fresh water worldwide. To meet the growing demand, non-typical sources of water have to be found. Water desalination is the main key option to provide the suitable supply of potable water. Recent estimates suggest that up to 25 million m<sup>3</sup> of desalinated water is produced daily worldwide (Lattemann & Höpner, 2008) of which almost two thirds is produced in countries in the Middle East and North Africa. In this area are located 77% of all desalination plants, whereas in the Asia-Pacific region, in the Americas and in Europe, there are 6, 7 and 10%, respectively (Lattemann & Höpner, 2008).

Desalination technologies can be divided in two main categories: thermal distillation (multi-stage flash, MSF and multiple effect distillation, MED) and membrane separation (reverse osmosis, RO). Hybrid plants integrating thermal and membrane processes also exist (Hamed, 2005). Other technologies that are of minor application include vapour compression (VC) and electrodialysis (ED). New engineering technologies, still under research and development, include capacitance deionization (CDI), membrane distillation (MD), forward osmosis (FO), gas hydrates (GH) and freezing, humidification dehumidification (HDH) (Mezher et al., 2010; Joint Water Reuse, Desalination Task Force [JWR & DTF], 2005).

The worldwide desalination capacity by process is shown in Fig. 1. Desalination plants use mostly seawater, followed by brackish, river and waste water (Fig. 1).

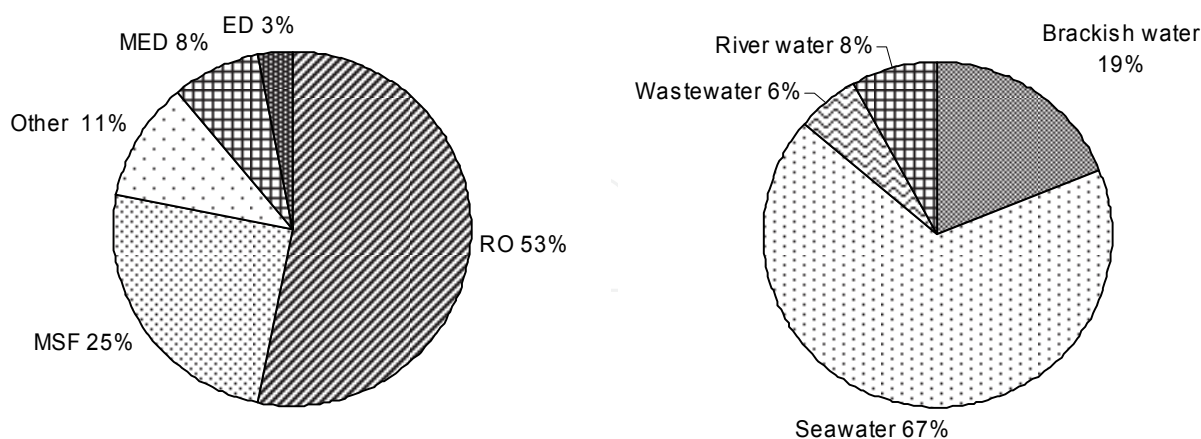


Fig. 1. Global desalination capacity by process (left) and worldwide feed water quality used in desalination (right) (ESCWA, 2009)

The importance and role of desalination do not deserve further comments. However, concerns are rising over strong potential negative impacts of desalination processes on the environment (Lattemann & Höpner, 2008; Maugin & Corsin, 2005; Miri & Chouikhi, 2005; Winters et al., 1979). The potential damages to the environment include: a) the uncontrolled

discharge of concentrated brines which can impair aquatic ecosystems and water quality of aquifers; b) air pollution due to carbon dioxide emissions related to the energy used in the desalination processes. Desalination plants produce fresh water and discharge high salinity water (reject water or brine). The brine flow rates are large and generally vary with the type of technology; they are up to 40% for RO and up to 90% for MSF of the intake flow rate (Mickley, 2010). The reject water is a concentrate stream having a salinity higher than source feed water, up to 65,000-85,000 mg L<sup>-1</sup> (Abdul-Wahab & Al-Weshahi, 2009), double or close to double that of natural seawater. The disposal of such a huge amount of high salinity water is one of the main environmental concerns. The brine may also have increased in temperature as values ranging from 5 to 15°C above intake waters may be reached (Lattemann & Höpner, 2008). Besides the high concentrations of salts, the brine contains residues of chemicals used for pre-treatment, by-products formed during the treatment, and heavy metals due to corrosion. The chemicals are used against scaling, biofouling, foaming, suspended solids and corrosion. The additives increase the detrimental impact of the brine as they are discharged along with the concentrate in the environment (Abdul-Wahab & Al-Weshahi, 2009; Lattemann & Höpner, 2008; Mezher et al., 2010).

In general, metal concentrations are low. However, copper in reject streams of thermal plants where Cu-Ni heat exchangers are used, can adversely affect the environment.

Several alternative approaches for handling the high salinity water exist (GHD, 2003; Lattemann & Höpner, 2008; Mezher et al., 2010; Mickley et al., 1993). The ways of disposing of the brine (Table 1) include deep well injection, land application, delivery to evaporation ponds, discharge in a sewer system, direct discharge to both surface water and submerged, aquaculture and beneficial re-use of the brine through salt recovery and harvesting systems.

Country	Disposal method
Qatar	Land application and evaporation ponds
Jordan	Land application and evaporation ponds
Oman	Land application and evaporation ponds
Kingdom of Saudi Arabia	Evaporation ponds
Australia	Evaporation ponds
Kuwait	Evaporation ponds
China	Land application
United Arab Emirates	Surface water
Spain	Surface water
Japan	Surface water
Algeria	Surface water
United Kingdom	Sewer system blending and land application
United States of America	Surface water, sewer system blending, land application, evaporation ponds, and deep well injection (in increasing order of % use)

Table 1. Disposal methods used by some countries (Mezher et al., 2010 and references therein)

The selection of a disposal method is influenced by different factors such as volume of brine, constituents, geographical location of the discharge point, availability of receiving site, permissibility of the approach, public acceptance, capital and operating costs, ability of the facility to be expanded, and economics of the recovered products (Abdul-Wahab & Al-Weshahi, 2009; Ahmed et al., 2001; Mickley et al., 1993).

The cost of the brine disposal plays an important role in the selection of the method (Economic and Social Commission for Western Asia [ESCWA], 1993) as it could range from 5 to 33% of the total cost of desalination (Mohamed et al., 2005).

In the last decade, there has been an increased awareness that the main limitation to the further development of desalination is represented by brine management, a term that allows for beneficial use and volume reduction of brine in addition to its direct disposal. The challenge is to change the concept from saline waste to saline resource opening several opportunities to provide a reduction of brine disposal costs and volumes involved. The beneficial uses reported in the literature include aquaculture, oil and gas well field injection to maintain pressures, feedstock for hypochlorite production, dust control and de-icing, soil remediation, zero liquid discharge, wetlands treatment, salt recovery, and solar ponds (e.g., Abdul-Wahab & Al-Weshahi, 2009; GHD, 2003; Mickley, 2010).

An innovative and non-traditional use of the brine is its involvement in several industrial processes with the dual beneficial objective to reduce its volume to be discharged and mitigate the negative effects of some contaminants such as CO<sub>2</sub> and animal waste.

## 2.2 The problem of carbon dioxide

Daily we are all bombarded by alarming news about the rising levels of CO<sub>2</sub> in the atmosphere, caused largely by the combustion of fossil fuels, and about the deleterious impact of such loadings on our climate. Currently, many groups are actively seeking practical ways to sequester CO<sub>2</sub> being produced industrially, and to mitigate the environmental impact due to the uncontrolled discharge of concentrated brines from desalination plants. According to the Third Assessment Report of the Intergovernmental Panel on Climate Change (IPCC) (Morita et al., 2001), with its proposal to stabilize the CO<sub>2</sub> concentration between 450 and 750 ppmv, cumulative emissions ranging from 220 to 2,200 GtCO<sub>2</sub> (60-600 GtC) would need to be attained during this century. With the continued growth of emerging densely populated countries like China and India, there is the prospect of tripling the loading of CO<sub>2</sub> to the atmosphere by the end of the 21<sup>st</sup> century.

Clearly, the scientific community must implement quickly the research on effective methods of sequestering CO<sub>2</sub>. All the approaches to reduce the global CO<sub>2</sub> emission must be examined carefully, even if most of them are not very encouraging as far as their quantitative potential to compensate for the huge amounts of fossil-fuel-derived CO<sub>2</sub> already in the atmosphere.

Numerous CO<sub>2</sub> sequestration approaches, including ocean, terrestrial, geological, biological and chemical options are currently being studied (Conrad & Klose, 1999; Freund & Ormerod, 1997; Friedmann, 2007; Gunter et al., 1997; Holloway, 1997; Lackner et al., 1995; Lackner et al., 1998; Lackner, 2003; Metz et al., 2005; O'Connor et al., 2002; Parson & Keith, 1998; Xu et al., 2004). As a substantial share of CO<sub>2</sub> emissions must be stored, the retention or sequestration of CO<sub>2</sub> in geological reservoirs is currently the applied option (e.g., Weyburn, Canada; Sleipner, North Sea; Holloway et al., 2007). Deep aquifers and depleted reservoirs in oil and gas fields have stored natural gas and crude oil for million of years. They thus offer possible sites for long-term storage of CO<sub>2</sub> (Gunter et al., 1997; Holloway, 1997). A variant of the depleted reservoir solution involves injecting



CO<sub>2</sub> in ultrabasic and basic rocks, such as might be encountered in ophiolitic complexes (Lackner et al., 1995; Robertson, 2004). These rocks are pervasively fractured owing to the tectonic forces active during their emplacement. However, the behaviour of CO<sub>2</sub> in such media, and the physical and chemical changes that can be expected in rocks if CO<sub>2</sub> is injected, are still a concern in the scientific community (Holloway et al., 2007; Huijgen et al., 2006).

The sequestration capacity of deep oceans is about 104 GtC (e.g., Freund & Ormerod, 1997; Lackner, 2003). The depth of injection would have to be ~1500 m, which raises serious technological challenges. This option could reduce the level of CO<sub>2</sub> in the atmosphere significantly. However, about 20% of injected gas can be expected to return to the atmosphere in ~300 years (Freund & Ormerod, 1997). Furthermore, the biological impact of such massive injection of CO<sub>2</sub> is of serious concern, as the resulting decrease in pH of seawater would most likely not be tolerated by the marine ecosystem (Freund & Ormerod, 1997; Lackner, 2003). In addition, there are thorny legal issues concerning disposal in the deep ocean, and possible catastrophic events during the injection process.

Existing photosynthetic systems naturally reduce the level of CO<sub>2</sub> in the atmosphere. They do not require pure CO<sub>2</sub>, and incur no costs for preparation of the reactants. However, unrealistic areas of land and ocean would have to be used and could hardly be expected to compensate for CO<sub>2</sub> emissions of a single power plant (Parson & Keith, 1998). Efforts are under way to develop non-photosynthetic microbiological processes capable of converting CO<sub>2</sub> into methane and acetates (Conrad & Klose, 1999). It is appropriate to recall the small-scale success of the Fischer-Tropsch reaction in converting CO and H<sub>2</sub> into an array of hydrocarbons by reaction with iron-rich minerals, most recently to supply the domestic needs of South Africa during the apartheid-related oil embargo (Marsh et al., 2002). Again, unrealistic amounts of solid reactants would be needed to have any impact whatsoever.

Complementary CO<sub>2</sub> retention technologies, such as mineral sequestration *via* reaction of CO<sub>2</sub> with Mg-Ca-silicate rocks and/or neoformation of carbonate minerals in aqueous solutions, are attractive for their permanent and safe CO<sub>2</sub> storage in a solid form (Soong et al., 2006).

The methods based on neoformation of carbonates or bicarbonates, requires cations to neutralize CO<sub>2</sub> (Lackner et al., 1995; O'Connor et al., 2002). If a supply of the appropriate cations can be assured, such carbonation reactions offer virtually unlimited capacity and the promise of safe, permanent storage of CO<sub>2</sub>. This idea was first proposed by Seifritz in 1990. There is little risk of unexpected release of CO<sub>2</sub> back to the atmosphere, because the resulting carbonates are thermodynamically stable (Ballirano et al., 2010; Ferrini et al., 2009). The process occurs naturally on a small scale during the weathering of rocks (Robertson, 2004), and has been shown to be important locally in ultrabasic and ophiolitic complexes (Hansen et al., 2005). The source of the neutralizing ions could be magnesium and calcium silicates such as olivine, serpentine-group minerals and clinopyroxene. Unfortunately, the industrial extraction of Ca and Mg from silicate minerals requires expensive pre-processing, which contributes to the problem rather than to the solution (Lackner et al., 1997). Furthermore, this option is not at all practical in many countries owing the paucity of exposed basic and ultrabasic rocks.

An attractive alternative would involve the interaction of ions in aqueous solution with CO<sub>2</sub>. In this case, the precipitation of carbonates of Ca and Mg proceeds much faster than if the cations are locked in a silicate structure. The source of such a process could be a brine

(Ferrini et al., 2009) or even seawater. There is an advantage in focusing on Mg, because a greater weight proportion of CO<sub>2</sub> is found in Mg carbonates than in Ca carbonates. The process represents a variant of the Solvay process (Lackner, 2002) and is based on carbonating alkaline brines, which would produce carbonates from a chloride-rich reactant and hydrochloric acid as a by-product (Lackner, 2002).

### 2.3 The problem of animal waste

Large quantities of animal waste are produced in millions of tonnes each year worldwide. The intensive scale of animal farming, indeed, produces a large amount of waste that must be discharged. For this reason their management is of great concern, as the improper management of manure can adversely affect soil, water and air quality due to leaching and run-off of organic constituents, nutrients and heavy metals (Hsu & Lo, 2001; Wadman et al., 1987). In traditional agriculture, as the animal wastes represented the main source of crop nutrient, they were re-used for this purpose, generating equilibrium between waste production and their re-use and discharge. Today, the development of modern agriculture and intensive breeding has broken this equilibrium.

The amount of animal waste produced commonly is greater than that disposable locally on agricultural soil with no risks to the groundwater. In recent years the demand for livestock and poultry production grew in both developed and developing countries (Yetilmezsoy & Sapci-Zengin, 2009). For example, the total amount of organic dry substance produced in Germany by about 16 million cattle, 26 million pigs, 114 million poultry and 4 million sheep and horses accounts for 57,500 tonnes organic dry substance in 2001, whereas in Japan the total amount of animal waste is about 90 million tonnes per year (Haga, 1998; Köttner, 2001). Manure production in Spain was about 190 million tonnes per year (Moral et al., 2008). The yearly production of poultry and livestock waste in Russia exceeds 700 million m<sup>3</sup> (Kalyuzhnyi et al., 1998). Moreover, in most developing countries the poultry production is rapidly growing; for example, in Nigeria the amounts of waste produced represents millions of tonnes.

The disposal of such huge amounts of animal waste while minimizing the impact on the environment is one of the most serious challenge facing modern agriculture. The discharge of nutrient-rich wastewater to the environment increases the risk of eutrophication of natural waters owing to high levels of phosphorus and nitrogen (Yetilmezsoy & Sapci-Zengin, 2009). The removal of P and N in water is now regulated in many countries, and minimal concentrations of P in effluents are imposed. In particular, the European Community Urban Waste Water Treatment Directive [EC UWWTD] 97/271/EC (1991) has dealt with this pollution problem (Doyle & Parsons, 2002). The processes for P removal are traditionally based on P fixation in activated sludge by a biological or chemical method. Anaerobic lagoons are widely used in the treatment of liquid manure (Vanotti et al., 2007). In general, these processes can reduce the concentration of P in wastewater effluents, but they cause the accumulation of this element in sludge as well as a net increase in the volumes of sludge (Le Corre et al., 2009). Moreover, environmental problems connected with this method of treatment include emission of ammonia, odours, pathogens, and the potential deterioration of water quality (Aneja et al., 2000; Loughrin et al., 2006; Mallin, 2000; Szogi et al., 2006; Vanotti et al., 2005). New options for nitrogen removal are based on the so-called anammox, the combination of partial nitrification and anaerobic ammonium oxidation (Hwang et al., 2005), but they are still under development.

Besides P and N, animal waste pose a further risk of contamination owing to their contents in heavy metals. High concentrations of Cu, Zn and Mn occur in manure as these elements are provided in feed because their antimicrobial and growth-stimulation effects (Kessler et al., 1994). Most of this metal load (in particular Cu and Zn) is largely added at levels exceeding physiological requirements (Jondreville et al., 2003) and therefore, they are excreted in animal slurry. The application of the manure to agricultural soil results in a significant loading in soils. Some authors reported contents of Cu and Zn up to 3.3 kg/ha and 2.2 kg/ha, respectively. In addition to these elements, Pb, Ni, Cr and Cd are also present in the animal diet in Western Europe; these elements have phytotoxic effects even at low concentrations.

The animal wastes, containing mainly phosphorus, ammonium-bound nitrogen and heavy metals, can usefully be involved in a process *via* mineralization aimed at the discharge of reject brines from desalination plants. The process offers a dual-purpose approach for the management of reject brines and the removal of P and  $\text{NH}_4\text{-N}$  from wastewater produced by biological industrial activities. Moreover, the recovery of P through the synthesis of P-bearing minerals could represent a highly competitive source of this element, alternative to the limited reserves of natural phosphate rocks.

### 3. Novel technological strategies

#### 3.1 Challenge 1: The role of reject brines in the sequestration of carbon dioxide *via* mineralization

Carbonation reactions are common in nature but the idea of developing this process for the disposal of  $\text{CO}_2$  based on the chemical fixation of the carbon dioxide in the form of carbonate minerals was only proposed in 90s using calcium in brines, and then by carbonation of magnesium-bearing minerals from ultramafic igneous rocks. There are serious problems with that approach: the reaction kinetics for magnesium silicates tends to be too slow, and environmental concerns are associated with mining and processing very large amounts of magnesium-bearing rocks.

Our group has recently described a carbonation process involving the reaction of gaseous  $\text{CO}_2$  with a magnesium chloride solution producing a hydrated carbonate stable at Earth surface conditions (Ferrini et al., 2009). Additional experiments intended to simulate more closely the reject brines that are industrially available have been performed to explore the influence of the salinity on the carbonation process. The results of the experimental work suggest that the goal of  $\text{CO}_2$  sequestration and reject brines discharge seems to be realistically obtained also using the more common saline wastewater. Moreover, the solid products and the by-products of the process can be applied in a large number of industrial processes, resulting in an attractive way safely manage hazardous wastewater and greenhouse gases.

##### 3.1.1 Reject brines disposal and $\text{CO}_2$ sequestration within carbonate minerals

Our initial work on the carbonation process involved a relatively dilute solution of magnesium chloride, roughly  $7 \text{ g L}^{-1}$  of Mg, at room temperature.

In fifty experiments we synthesized carbonates of Mg using  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  as a source of magnesium and sparging  $\text{CO}_2$  through the Mg chloride solution. The time of interaction of the flux of  $\text{CO}_2$  with the solution was prolonged until the point of saturation of the solution in  $\text{CO}_2$ , as suggested by the stabilization of pH values.



The reaction rate was found to be rapid, the deposition of nesquehonite,  $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$ , being virtually complete in about ten minutes (Fig. 2) according to the following reaction.

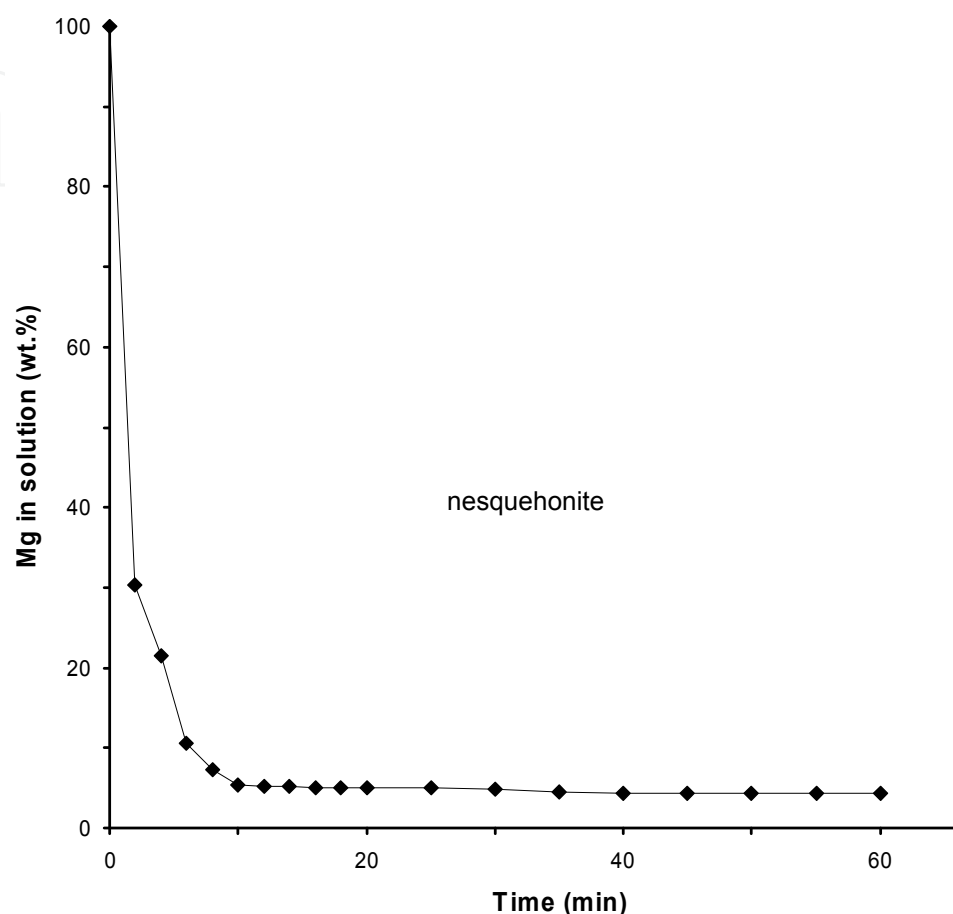
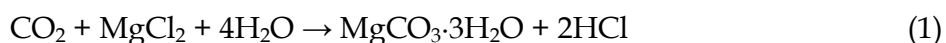


Fig. 2. Kinetics of the carbonation reactions

Nesquehonite removed about 80% of the carbon dioxide in solution, and the pH of the solution, adjusted by adding ammonia solution (25%), was made to range at an optimum value between 7.8 and 8.2.

To test the efficiency of the carbonation process in more concentrated solutions, having salinity more close to that of the reject brines, further experiments have been carried out using solutions with different degree of salinity (16 and 32 g L<sup>-1</sup> of Mg).

A comparison of the efficiency of the CO<sub>2</sub> mineralization process among sets of experiments performed at low and high salinity shows that in more concentrated solutions, the efficiency was reduced to about 65%.

It is known that the degree to which CO<sub>2</sub> dissolves in water is determined by the solubility constant  $K_0 = [\text{CO}_2^*]/[\text{CO}_{2(g)}]$ , where CO<sub>2</sub>\* is the sum of the species CO<sub>2(aq)</sub> and H<sub>2</sub>CO<sub>3(aq)</sub> (Moran, 2010). The constant K<sub>0</sub> depends on temperature, pressure, salinity and the ionic composition of the water. The increase of the temperature favours the gas phase and shifts reaction (2) to the left, as will an increase in salinity of the electrolyte solution, whereas increasing pressure results in higher solubility of CO<sub>2</sub>.



Moreover, the presence of different salts in the solution reduces the solubility of  $\text{CO}_2$  in the solution and this decrease is known as the “salting out effect” (Yasunishi & Yoshida, 1979; Al-Anezi et al., 2008). Adding large quantities of  $\text{MgCl}_2$  creates a network of hydrogen bonds with  $\text{H}_2\text{O}$  molecules that shifts the equilibria (2) and (3) toward the left.



This reduction in the solubility of  $\text{CO}_2$  would seem to significantly reduce the efficiency of the process. In fact, with a more concentrated solution of magnesium chloride, the residence time of  $\text{CO}_2$  is enhanced in the aqueous medium because of a reduced tendency to produce  $\text{CO}_{2(\text{g})}$ . At equivalent  $\text{CO}_2$  contents, the more saline the solution, the less effective is the loss of the gas phase. The low degree of  $\text{CO}_2$  degassing results in a longer-term availability of carbonic ions to react with  $\text{Mg}$  ions to form stable carbonate minerals (Mignardi et al., 2011).

### 3.1.2 Stability of nesquehonite

Nesquehonite occurs as a low-temperature carbonate in alkaline soils, in cave deposits and as a weathering product of ultramafic rocks.

Nesquehonite is a monoclinic hydrated carbonate of  $\text{Mg}$  and its structure consists of infinite flat ribbons of corner-sharing  $\text{MgO}_6$  octahedra along the **b** axis of the crystal, which is the fiber axis, linked by hydrogen bonds. Within the chains,  $\text{CO}_3$  groups link three  $\text{MgO}_6$  octahedra by one edge and two common corners. The  $\text{Mg}$  atoms are in a distorted coordination, and each atom is coordinated by two  $\text{H}_2\text{O}$  ligands; one free  $\text{H}_2\text{O}$  molecule is located between the chains (Giester et al., 2000).

In order to evaluate the appropriateness of a reaction of  $\text{CO}_2$  with  $\text{Mg}$  chloride solutions as a process for storing carbon dioxide and wastewater, the thermal behaviour of nesquehonite was investigated *in situ* using real-time parallel-beam X-ray powder diffraction. Nesquehonite appears to be stable up to 373 K (Ballirano et al., 2010) suggesting that its storage as “sequestering medium of  $\text{CO}_2$  and reject brines” remains stable under the temperature conditions that prevail at the Earth’s surface. At temperature above 373 K the process of thermal decomposition of nesquehonite (*via* intermediate hydrated magnesium carbonate phases) ultimately produces magnesite in the range 423–483 K. This sequence involves the formation of carbonate minerals thermodynamically more stable than nesquehonite, assuring the stable storage of these hazardous materials for millions of years.

According to information in the literature, no appreciable  $\text{CO}_2$  release will occur if  $\text{Mg}$  hydrate carbonates are leached in solution having  $\text{pH} > 2$ . Because the  $\text{pH}$  of acid rain is unlikely to be below 2.5, the possible release of  $\text{CO}_2$  from sites of nesquehonite storage due to acid rain should be unimportant.

### 3.1.3 Nesquehonite could be an ideal starting point for a manmade and environmentally safe supply of carbonate

The sequestration of  $\text{CO}_2$  and the disposal of reject brines *via* carbonation produces a solid material that can be utilized directly in many products such as acoustic panels, non structural panels, insulation, or agglomerated in concrete as a manmade aggregate.

Because nesquehonite grows as fibrous and acicular crystals (Fig. 3), it improves the microstructures of manufacturing materials.

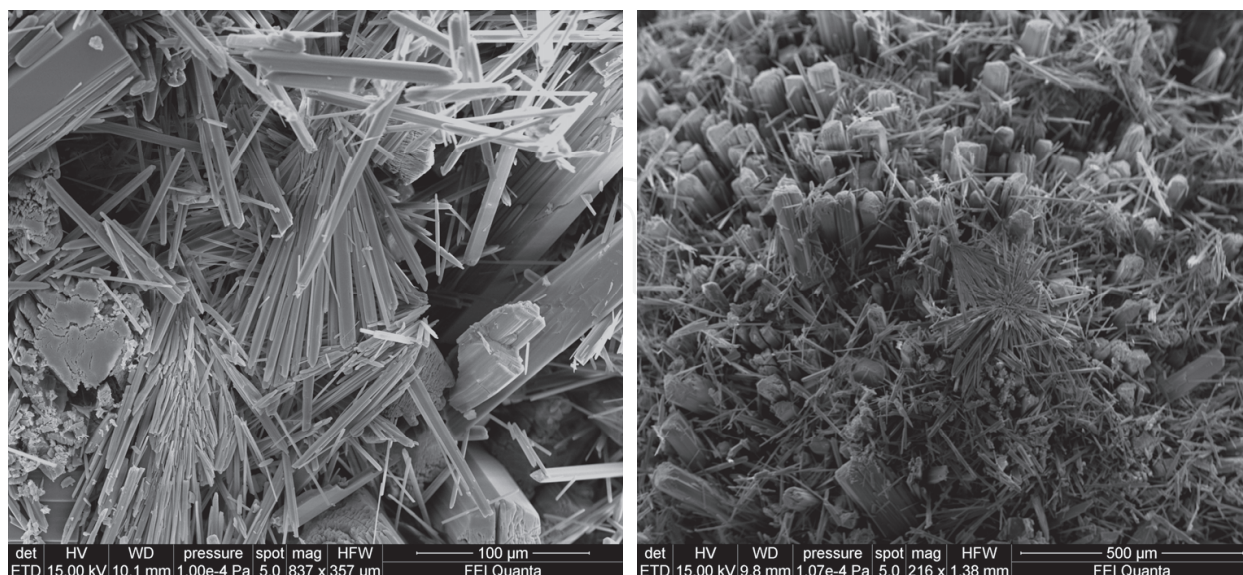


Fig. 3. SEM images of synthetic nesquehonite

### 3.2 Challenge 2: The role of reject brines to contribute to the abatement of the massive discharge of animal waste

The treatment of waste from animal farming represents a considerable problem from environmental and economic points of view. Indeed, the uncontrolled discharge of these wastes is generally regarded as the primary source of pollutants responsible for eutrophication of rivers and lakes.

Numerous approaches to P and N removal, including chemical precipitation, biological removal, crystallization, tertiary filtration, and ion exchange (Morse et al., 1998) are currently being applied.

The crystallization of P and N as struvite (magnesium ammonium phosphate,  $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ ) is one of the option most promising to remove both P and N. It has been applied in various countries for the treatment, for example, of swine waste (Burns et al., 2001; Nelson et al., 2003) and agro-industrial effluents (Altinbas et al., 2002).

The precipitation of struvite and other complex phosphates in wastewater treatment plants was already identified in the last century, but the development of an *ex situ* methodology based on the direct synthesis of these mineral phases for the treatment of both saline and animal waste has not been explored so far.

#### 3.2.1 Reject brines and animal waste disposal within phosphate minerals

Our research group recently approached the problem of phosphorus and nitrogen removal from animal waste by developing a process of mineral synthesis using solutions involving both slurries and reject brines. In particular, the process was applied to a mixture composed by anaerobic lagoon-based swine slurry and simulated reject brine. The concentration of P and  $\text{NH}_4\text{-N}$  in the slurries ranged from about 160 to 200  $\text{mg L}^{-1}$  and 600 to 2150  $\text{mg L}^{-1}$ , respectively; whereas the reject brine was a magnesium chloride solution ( $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ ) having 32  $\text{g L}^{-1}$  of Mg. The  $\text{Mg}^{2+}:\text{PO}_4^{3-}$  molar ratio was adjusted to 1:1. The suitable range of

pH for the phosphates precipitation ( $\sim 9$ ) in our experimental conditions was obtained by adding ammonia solution (25%  $\text{NH}_3$ ). The solution was thoroughly mixed using a magnetic stir plate at room temperature. The reaction rate was rapid, with solid product formation almost complete in few minutes.

The XRD pattern of the precipitates was found to be in good agreement with that of struvite (Fig. 4). Well-formed crystals (Fig. 5) are greyish; their formation occurred according to reaction (4).



However, this equation is a simplification of the reaction involved in struvite precipitation.

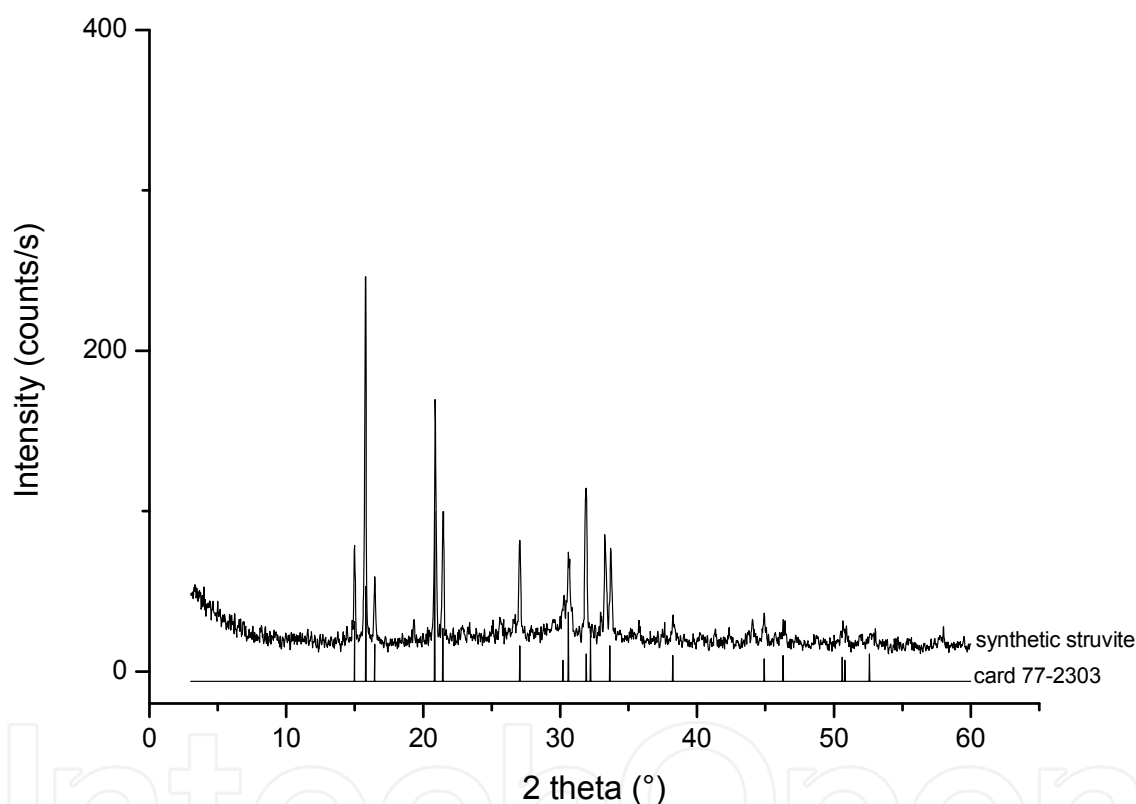


Fig. 4. XRD pattern of synthetic struvite compared with the strongest lines recorded in JCPDS card 77-2303

Indeed, the crystallization of struvite is controlled by pH, temperature, supersaturation of the reactants, and also the presence of calcium in the solution. However, the low concentration of calcium in the treated slurry did not affect negatively the formation of struvite in our experiments.

The synthesis of struvite efficiently removed P (never less than  $\sim 75\%$  in fifteen experiments) and as the molar ratio  $\text{NH}_4^+/\text{PO}_4^{3-}$  is  $\gg 1$ , the precipitation of struvite left an ammonium chloride- $\text{H}_2\text{O}$  mixture as a residual solution. This solution can be used economically to prepare crystalline ammonium chloride.



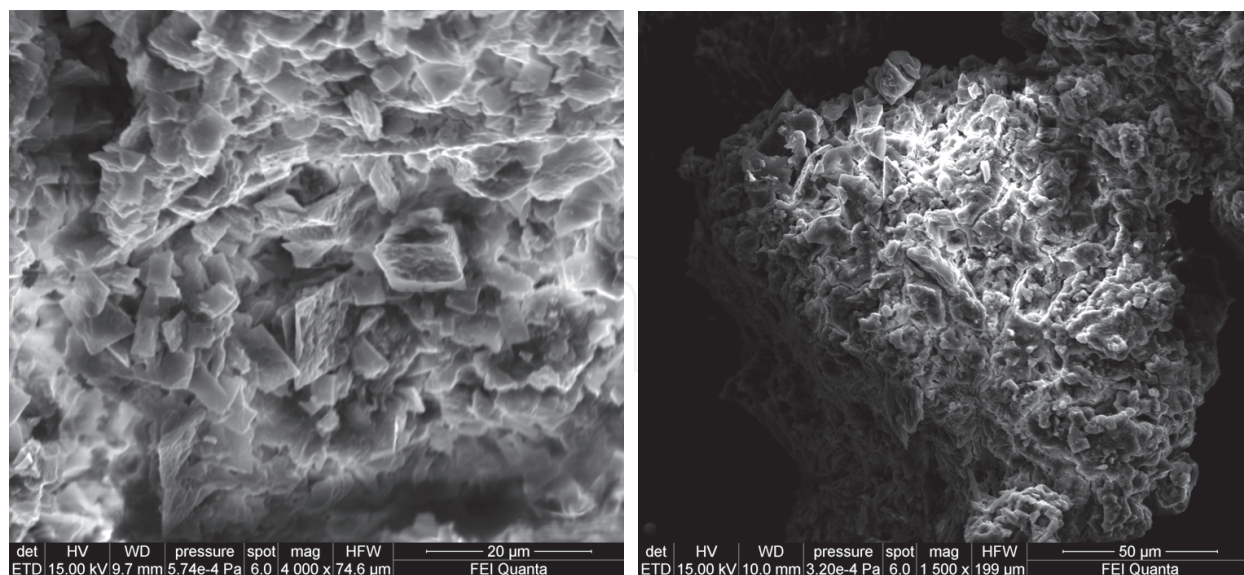


Fig. 5. SEM images of synthetic struvite

### 3.2.2 Struvite formation in the management of reject brines and animal waste

The synthesis of struvite can be considered as a suitable alternative for the treatment of animal waste and reject brines as it is a relatively inexpensive and effective technology. The results of our experimental work along with those reported in the literature, suggest that the abatement of P and  $\text{NH}_4\text{-N}$  *via* mineralization is technically and operationally feasible. However, as the composition of animal waste in term of P and  $\text{NH}_4\text{-N}$  concentrations is extremely variable, the treatment *via* struvite formation must be carefully adapted to the actual composition of the waste to be managed. Indeed, on the basis of the  $\text{NH}_4\text{-N/P}$  molar ratio, in an ideal solution having a ratio 1:1, the process would achieve the almost complete abatement of these contaminants. Moreover, as slurries with low concentration of P also exist, other P-bearing wastes for the formation of struvite should be involved in the process. In this way, alternative P sources include streams from corrosion treatment of iron metals, domestic sewage, and detergent and agricultural effluents (Verma et al., 2007).

Where high concentrations of Ca ions are present in the solution, calcium phosphate will preferentially precipitate, and cause a reduction in the yield of struvite. However, calcium phosphates also remove P and can be used for agricultural applications, just as struvite.

The synthetic phosphates produced using the method described above represent environmentally friendly resources, as their formation is based on the re-use of by-products whose regulatory standards for their discharge are becoming very stringent. They are also economically important as fertilizers.

### 3.2.3 Synthetic struvite as a resource

The abatement of P and N *via* mineralization produces a solid material, i.e., struvite, which offers numerous advantages. It is an excellent fertilizer compared with those normally used (Ghosh et al., 1996). Its agronomic qualities include: low solubility in water, resulting in the prolonged release of nutrients during the growing season, without danger of burning roots of crops treated, highly effective source of nutrients (P, N, and Mg) for plants, and the addition of possible supplements as micronutrients.



Global reserves of high quality phosphate ore are forecast to be exhausted by the end of the century, resulting in increasing prices and environmental impacts from the processing of ore reserves of lesser quality or more difficult access. Therefore, the possible recovery of P from wastewater could become an increasingly appealing opportunity (Gaterell et al., 2000).

Another incentive for the treatment of slurries through the formation of struvite is the important reduction in the volume of sludge to be discharged.

#### 4. Future research

The results of our experimental work have highlighted the potential of reject brines as a source of several elements to be involved in processes contributing to the development of environmental technologies.

*Challenge 1* - Future research should focus on the efficiency of the carbonation process starting from multi-elemental solutions, simulating the composition of reject brines now being produced industrially. In particular, we shall investigate the carbonation process using brines with elevated concentrations of sodium and aluminium for the synthesis of dawsonite,  $\text{NaAl}(\text{CO}_3)(\text{OH})_2$ . This hydrated carbonate occurs in nature as aggregates of acicular to fibrous crystals in several sedimentary sequences and in various depositional environments (e.g., associated with eruptive rocks, derived but not directly associated with magmatic rocks, and related to hydrothermal mineralization; Baker et al., 1995; Ferrini et al., 2003; Sirbescu & Nabelek, 2003).

Dawsonite has been successfully synthesized as a way to deal with the etching waste streams of the aluminium anodizing industry, in order to reduce the emissions to the environment and also to recover a useful and marketable mineral resource (Alvarez-Ayuso & Nugteren, 2005).

Most investigators dealing with the reactions involved in the injection of  $\text{CO}_2$  into deep sedimentary formations hypothesize the formation of various carbonate minerals, including dawsonite. Therefore, any information about the mechanisms and kinetics of the formation of this carbonate in aqueous solution should be utilized to determine the potential of a process aimed at sequestering  $\text{CO}_2$  involving Na-enriched reject brines and Al-bearing wastewater.

*Challenge 2* - To assess the possible use of synthesized struvite as an agricultural fertilizer, an evaluation of its heavy metal content (e.g., Pb, Zn, Cu, Cd, Cr, Fe, and Ni) will be of critical importance. The presence of such pollutants in fertilizers is strictly regulated and excessive amounts can result in the fertilizer being banned from use in agriculture.

A rather limited number of previous studies on the quality evaluation of struvite in terms of heavy metal content exist in the literature. Therefore, our research will be focused on the synthesis of struvite using for the reactions slurries having various concentrations of toxic metals with the objective to test the maximum concentrations of these elements that can be hosted in the structure of struvite.

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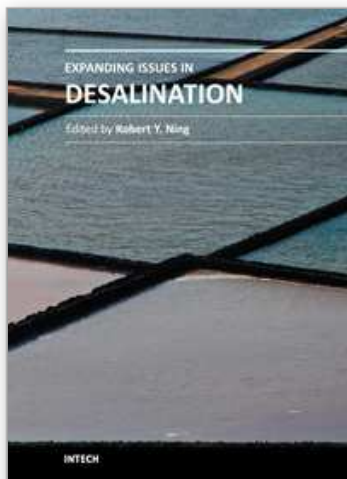


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## **Expanding Issues in Desalination**

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For this book, the term “desalination” is used in the broadest sense of the removal of dissolved, suspended, visible and invisible impurities in seawater, brackish water and wastewater, to make them drinkable, or pure enough for industrial applications like in the processes for the production of steam, power, pharmaceuticals and microelectronics, or simply for discharge back into the environment. This book is a companion volume to “Desalination, Trends and Technologies”, INTECH, 2011, expanding on the extension of seawater desalination to brackish and wastewater desalination applications, and associated technical issues. For students and workers in the field of desalination, this book provides a summary of key concepts and keywords with which detailed information may be gathered through internet search engines. Papers and reviews collected in this volume covers the spectrum of topics on the desalination of water, too broad to delve into in depth. The literature citations in these papers serve to fill in gaps in the coverage of this book. Contributions to the knowledge-base of desalination is expected to continue to grow exponentially in the coming years.

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