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Salt in the Earth

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Meet the editors



Prof. Dr Mualla Cengiz has been working at the Istanbul University, Cerrahpaşa, Department of Geophysical Engineering since 2000. She works on paleomagnetism applied on the tectonic assemblages of Anatolia and its surrounding area. She gives lectures in gravimety, earth magnetism, rock magnetism, and environmental magnetism. She has authored many international publications and collaborated in several national/inter-

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Preface

This book, "Salt in the Earth", contains four sections. Section I is titled "The importance of salt in water usage" and it includes the study "Delineation of salt-water and fresh water interface between Kolleru Lake and Bay of Bengal coast, Andhra Pradesh, India, using remote sensing and GIS techniques" by Harikrishna Karanam. The author showed that seawater intrusion areas could be successful found using integrated data of hydrogeology, hydrochemistry, remote sensing, and geophysical investigations.

Section II is titled "Salt intake in human life" and this section contains two chapters. The first chapter is "The role of salt on food and human health" by Miguel Elias, Marta Laranjo, Ana Cristina Agulheiro-Santos, and Maria Eduarda Potes. This chapter reports on the social and economic importance of salt throughout human history. The second chapter is on the "Systematic reduction of excessive salt intake" by Boris Kovač and Urška Blaznik and this describes the importance of salt intake and the importance of salt reduction in food.

Section III covers the main topic "Salt in technology" with two chapters. The first chapter, "Short review of salt recovery from reverse osmosis rejects" by Boopathy Ramasamy, covers some aspects of the route of water recovery. The author describes common methods to treat saline streams. The second chapter, "Upward capillary mass transfer as a process for growing concentration zones" by Alexandr Mikhailov, Ivan I. Vashlaev, Margarita Yu Kharitonova, and Margarita L. Sviridova, shows the advantages of the phenomenon of surface salinization of the soil layer. The chapter presents the results of experimental studies of ascending mass transfer of useful components from the waste material of the concentrating production of nonferrous metals.

Section IV, "The importance of salt in road safety", includes the chapter "NaCl material for winter maintenance and its environmental effect" by Durickovic Ivana. In this chapter, the effects of road salts used as a deicer during winter maintenance were investigated along with its chemical properties. The study is supported in general by many different methods with different examples and a wide literature background.

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Section 1

The Importance of Salt in Water Usage

Chapter 1

Delineation of Salt Water and Fresh Water Interface between Kolleru Lake and Bay of Bengal Coast, Andhra Pradesh, India – Using Remote Sensing and GIS Techniques

Harikrishna Karanam

Abstract

Kolleru Lake is the largest natural fresh water lake located between Godavari and Krishna deltas in Andhra Pradesh in India and is acting as a natural flood balancing reservoir. Dynamic land use changes from lake bed and agricultural land to aqua-culture and overexploitation of groundwater are becoming the major causes for salt-water intrusion. Changing of land use patterns is highly influencing on the quality of water. Paleo beach ridges are having potential aquifers around the Kolleru Lake. The main aim of this study is to identify seawater intrusion areas and reasons for intrusion. Integrated study of hydrogeology, hydrochemistry, remote sensing and geophysical investigations exposed the extent of salt-water intrusion up to the northern part of the lake, which is about 42 km away from the Bay of Bengal coast line. Top layer resistivity is more than 10 ohm-m in case of sand formations, 2-10 ohm-m in case of brackish water saturated formations and less than 1.0 ohm-m in case of saline water saturation aquifers, and clay-rich layers shows the resistivity in the range of 2 to 5 ohm-m. Remote sensing data and GIS (Geographical Information System) helped us to trace two major sea water intrusion patches from the coast to the lake.

Keywords: Kolleru Lake, saltwater intrusion, overly techniques, remote sensing and GIS

1. Introduction

Kolleru is one of the biggest shallow fresh water lakes in India which is located between the deltas of Godavari and Krishna Rivers of the Andhra Pradesh, India. The lake collects water by over 69 inflowing drains and channels. The catchment of Kolleru Lake is extends upto 9036.30 km². The major occupation of the surrounding people is agriculture and fishing. Since last three decades aquaculture is developed inside the coastal area encroached into the agricultural lands and into the Kolleru Lake also [1]. The main drinking water source to this area people is ground water. Potable groundwater is available in beach ridges in the range of 3–5 m depth and many houses having an open well. An endeavor is made to know the problem with multidisciplinary loom to propose some elucidation to develop the drinking water situation particularly the area between lake and the coast area.

Prolonged water logging conditions during the active monsoon periods due to poor drainage is not uncommon. Especially in drought time these wetlands are the best source to ground water potential and will play a major role in flood control at the time of active monsoon. Over past six decades the shifting of fresh water lake to agriculture land; and agriculture to aquaculture; and finally finishing to the aquaculture demolition was driven by the demanded economic benefit surpassing ecological and social community growth. Saltwater intrusion is adulterated coastal aquifers predominantly in and around the Kolleru lake region, most of the farmers to get aquaculture as an extracommercial source of income, where salt water is used from the nearby creaks [2]. Saline or brackish groundwater is present below fresh groundwater in deltaic and coastal areas [3]. Due to overexploitation of groundwater in many parts of India and worldwide the coastal aquifers are generally fragile in nature and the shallow aquifers are easily depleted [4]. Remote sensing and geophysical, geochemical and GIS techniques are used to directly or indirectly supervise saltwater in coastal aquifers. However, high TDS (Total dissolved solids) concentration or specific conductance of groundwater samples are other indicators of groundwater salinity [5]. Electrical Resistivity survey is the best method to discriminate the sub-surface layers includes aquifers and to certain extent the quality of groundwater [6]. Through the spatial distribution of electrical conductivity, we can assess the presence of dissolved ions in a coastal aquifer [7].

2. Study area

The study area lies in between the delta regions of Krishna and Godavari rivers which covers 31 revenue blocks (Mandals) out of that 16 revenue blocks in West Godavari district and 15 revenue blocks in Krishna district of Andhra Pradesh, India. The total area covered in this study is about 3861.97 km² lying in between 80° 50′ to 81° 39′ E longitude and 16° 17′ to 16° 59' N latitude. Location map of the study area is shown in **Figure 1**.

2.1 Geology

The study area is engaged by recent alluvium and forms a part of Krishna and Godavari deltas. Deltas are the results of the continuous supply of sediment by rivers to coasts and upper continental shelves. They make the largest latent places for the clastic sediments and the shape is mostly a lobe like extension of the coast with a number of divisions. The main axes of the delta run typical to the regional depositional strike. In general the area is occupied by clays, silts, silty clays and silty sands with variable thickness ranging from 1.5 to 3.5 m. These are under laid by sandy layers of variable thickness ranging from 1.5 to 4.5 m in the beach ridge regions and paleochannels. The deltaic plains are occupied by clays and silty clays and extend to a maximum depth of about 2 m. These clays are under laid by saturated clay deposits extending up to greater depths. Main geological features in this study area are active beach, flood plain, Gollapalli formation, Gollapalli/ Chintalapudi sandstone, khondalite, Kolleru formation, Kolleru Lake, laterite, paleo beach ridges, paleo channel, paleo tidal flat, Rajahmundry sandstone and Tirupati

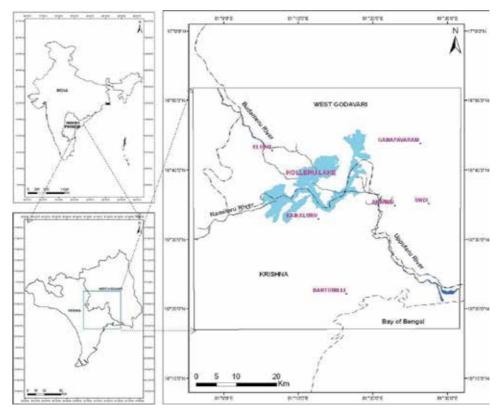


Figure 1. *Location map of the study area.*

sandstone and the geology map of the investigation area is shown in **Figure 2**. The geometry of the Kolleru-Upputeru catchment is guided by the regional lineaments. The most dominant directions of these lineaments are NW-SE and NE–SW. The density of fractures/lineaments is more in Archaean metamorphic rocks and Gondwanas of Chintalapudi sub-basin than East-coast Gondwanas and Rajahmundry sandstones. The structures in the area control the occurrence and movement of ground water.

3. Methodology

The methods adopted during the course of this investigation have been presented below. Standard scientific methods were used for laboratory investigation. The methodology has been presented as follows.

- Remote Sensing methods
- Integration of chemical data
- Electrical Resistivity survey
- Interpretation of field data and integration

Salt in the Earth

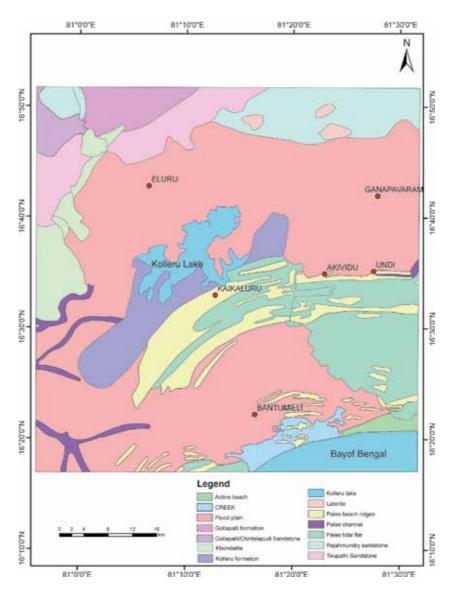


Figure 2. *Geology map of the study area.*

3.1 Remote sensing methods

Remote sensing has become the most powerful scientific tool for the study of various Earth resources and related features. The advent of colored satellite imageries has revolutionized the Remote Sensing activity. Survey of India toposheets of 1:50,000 scale maps were Geo-referenced than mosaic all the images in order and choose AOI (Area of Interest) with sub setting images (65D/13, 65D/14, 65D/15, 65H/1, 65H/2, 65H/3, 65H/4, 65H/5, 65H/6, 65H/7, 65H/8, 65H/9, 65H/10, and 65H/11) was done to extract the study area. IRS P6 LISS IV of March, 2014 digital satellite data is used for land use/land cover, geology and geomorphology studies.

3.1.1 Geomorphology

The major geomorphological features are flood plain deposition, lake bed, beach ridges and marine built plains are shown in **Figure 3**. Ridges are having potable

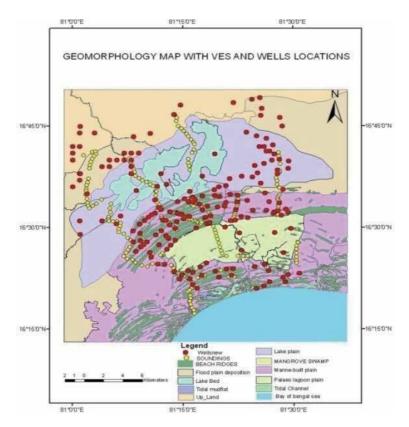


Figure 3. Wells and VES locations on geomorphology map.

fresh groundwater and shallow areas are deposited with saltwater. Almost all five strand lines are indicated that beach is slowly move away from the lake since Holocene period.

3.1.2 Hydrogeology

Totally 175 wells were selected to observe the groundwater table fluctuations for three continuous year during the research period and collected 175 water samples which covers the total study area and the locations of these wells are presented on the geomorphology map as shown in **Figure 3**. Water levels are measured with automatic water level indicator and coordinates were measured with Global positioning system (GPS) and 50% of the wells indicated more than 3.0 m depth of water table during pre-monsoon period.

3.1.3 Land use/land cover dynamics

The land use/ land cover map evidently shows that agricultural land is higher than others shown in **Figure 4a**. But since two decades aquaculture is abundantly increasing (**Figure 4b**). The results shows that the Kolleru lake in and around has good aquaculture potential (27.91% of TGA aquaculture) and agricultural land is 60.72% (include plantations, fallow land and horticulture) total geographical area of the study area. The land use/land cover categories like extent of the lake, aquaculture, cropland, and built-up land are mapped for 1985 and 2013 "**Figure 4a** and **b**". A buffer of 1 km interval is drawn from lake to 5 km. It is observed that the area under aquaculture within the lake has gradually increased (128 km²) till 2005.

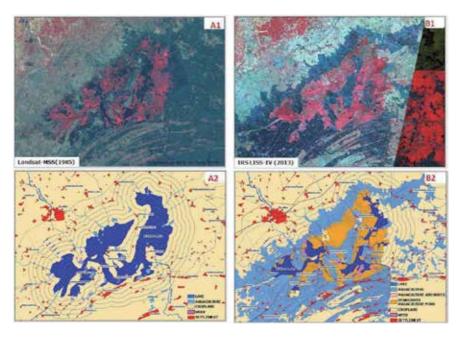


Figure 4.

(a) Dynamic land use changes within and around the lake during -1985; (b) dynamic land use changes within and around the lake during -2013.

3.1.4 Hydrology

The area is drained by five major hydrological systems that include Budameru, Ramileru, Tammileru, Gunderu and Errakalava of which the first four directly flow and let water into Kolleru whereas, Errakalava linked near to the mouth of Upputeru by construction of Enamadurru drain and thus falls into Upputeru Subcatchment. These rivers are ephemeral in nature and flow in response to rainfall and are influent to effluent in nature. The hydrological system depicting the Kolleru-Upputeru catchment and their watersheds is shown in **Figure 5**.

3.2 Integration of chemical data

Chemical parameters of groundwater samples are well explained above comparing the WHO and BIS standards [8, 9]. Broadly the areas of maximum desirable, maximum permissible and beyond permissible limits are demarcated. Red boundary line enclosure in **Figure 6** is highest TDS area. Same area with same geographical coordinates superposed over the thematic maps of all over the other 8 parameters like Electrical conductivity, salinity, Chlorides, Sodium, Hardness, Potassium, Calcium and Magnesium. **Figure 6(a)** is the areal distribution of TDS and **Figure 6(b)** is the aerial distribution of Ca over which the border line of beyond allowable limit of TDS is super posed. Similarly TDS is superposed over the other six parameters. Surprisingly all the chemical parameters high concentration is showing in two patches.

3.3 Resistivity survey

Electrical resistivity survey is one of the best technique to demarcate aquifer composition, groundwater, bedrock, and fresh/salt zones [10]. To delineating the

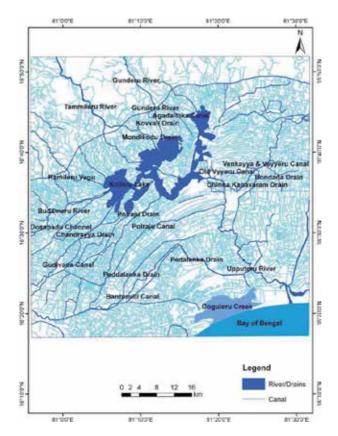


Figure 5. *Hydrological map of Kolleru catchment.*

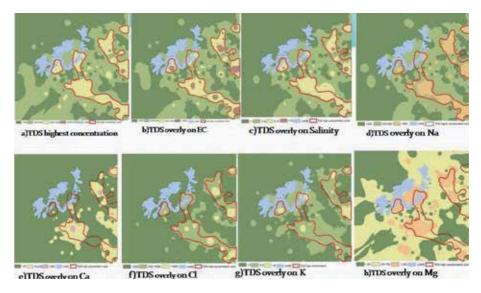


Figure 6.

Comparison of TDS high concentrations with other parameters.

shallow and deep aquifers using with Schlumberger configuration were made in the recent past [11, 12]. In this work the same method has been utilized to demarcate interface of different natures of water. The additional leaky or fissured a rock,

the lower the resistivity. Higher degree of saturation or greater amount of water presents in pore spaces and fissures also decreases the resistivity [13].

Top soils are having resistivity varies between 3 and 68 ohm-m in paleo beach ridges, lake plain and uplands. Flood plain deposition, marine lagoon plain and marine built plain having top soil resistivity varies between 2 to 27, 1 to 15 and 0.3 to 15 ohm-m, respectively. Paleo beach ridges which are having fresh potable water is having top soil resistivity between 8 and 50 ohm m. Spatial distribution of top layer resistivity has shown in **Figure 7**.

In the present chapter, geophysical resistivity studies and chemical analyses of ground water of different open wells are compared. Finally, an attempt made to compared analysis of Vertical Electrical Soundings (VES) data and chemical data of observation wells nearby sounding resistivity location which are more related.

3.4 Integration

Geographical Information system (GIS) is one of the best tool to identify salt water intrusion zones [14]. The heavy concentration of saltwater in ground water is represented the form of a map using weighted overlay techniques of ArcGIS.

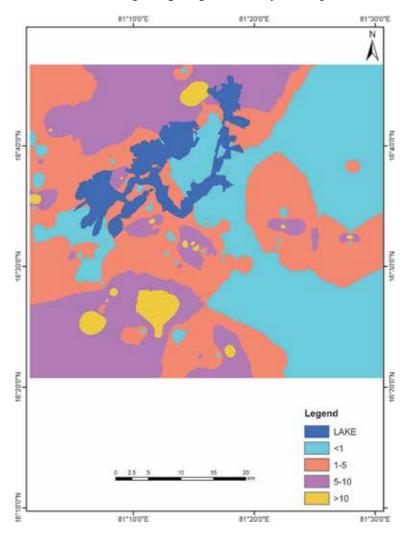


Figure 7. Spatial distribution of top layer resistivity.

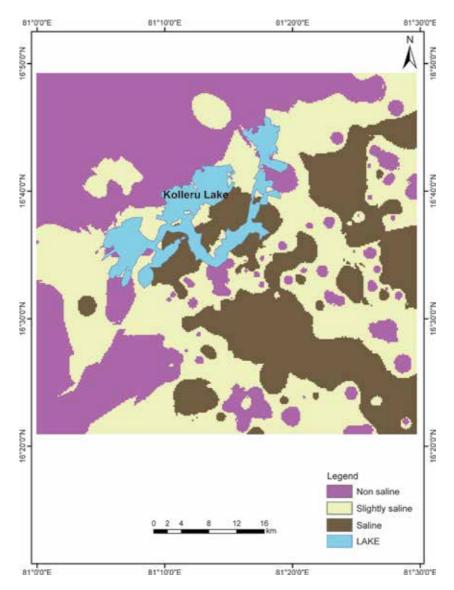


Figure 8. Broad classification of groundwater as per the integration of hydrochemical data and electrical resistivity.

Another important aspect of geographic information system (GIS) is that it enables the analysis of the spatial data and their attributes contained in the database. We have analyzed all the data layers through the process called "Overlay" in ArcGIS 9.3. Index Overlay is a best spatial action in which superimposed of many thematic layers onto another to form a new layer. This kind of overlay is also called "Arithmetic overlay," which means that values assigned to two or more input themes are combined arithmetically (+, -, *, /) to produce an output grid [15].

In this case the map classes exciting on each input layers are assigned different scores, as well as the maps have to assign different weights as before. It is suitable to describe the scores in an attribute Table for each input map. The averages score is than defined by the equation

$$\overline{s} = \frac{\sum_{i}^{n} s_{ij} w_{i}}{\sum_{i}^{n} w_{i}}$$

where

 \overline{s} = Weighted score for an area object (polygon, pixels)

 S_{ij} = Score for the j-th class of the i-th map

W_i = Weighted score for the i-th map

Binary map analysis, Fuzzy logic and Index Overlay with Multi-class maps are some other methods available to determine inter class dependencies or inter map dependencies. Here an attempt has been made to use multi class maps in Index overlay method [16].

The input layers which are considered for the analysis of groundwater vulnerability zones are Salinity, TDS, Resistivity, EC, TH, Na, Cl, Ca, Mg, K, N0₃, S0₄, TA and P^{H} .

To calculate sum of weighted conditions and divided by normalization factor

New Vulnerability Map = $\frac{[*Ml + *M2 + *M3 + *M4 + *M5 + *M6 + *M7 + *M8 + *M9 + *M10 + *M11 + *M12 + *M13 + *M14]}{SUM}$

According to the levels of concentrations of these chemical parameters and resistivity of the top layer in the study area these were given with a fastidious weightage number and operated to obtain a map which is used for further analysis. Hence, calculated the each grid cell data and represented in the form of map showing the saline and non-saline groundwater zones in **Figure 8**. Fresh ground water is available in uplands, flood plains and paleo beach ridge zones. The areas of paleo lagoons (**Figure 8**), marine plains, marine marshy lands shown in the non potable groundwater zones. Saline groundwater zones broaden into the lake area and the continuous big brown patch between lake and the coast may be the main route of salt water intrusion towards the land. There are several potable groundwater and the fresh water.

4. Conclusion

The results of this study clearly indicate that the sea water intrusion is taking place on both sides of the Kolleru lake through paleo channels. One big seawater intrusion zone was identified along the Upputeru river of 40 Km length from the coast to Lake. 70 out of 174 groundwater samples are non saline (40.2%), 37 samples are slightly saline (21.3%) and 67 samples are saline (38.5%). These statistics shows that potable groundwater is present in 40% of the total well locations. Most of the freshwater wells existed in the uplands of Kolleru Lake. Iso-resistivity contours of vertical cross sections clearly indicate the fresh and salt water zones. Areal mapping of fresh water aquifers (2023 sq.km) and sea water intrusion (784 sq.km) are also demarcated.

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Section 2

Salt Intake in Human Life

Chapter 2

The Role of Salt on Food and Human Health

Miguel Elias, Marta Laranjo, Ana Cristina Agulheiro-Santos and Maria Eduarda Potes

Abstract

Throughout time, salt (sodium chloride) played an important role in human societies. In ancient times, salt was used as a form of currency and to preserve foods, such as meat and fish. Besides, salt also assumed a major importance as food flavour enhancer. However, excessive salt consumption could result in serious health problems, related with hypertension and cardiovascular diseases, although this might be a controversial topic in the near future. The World Health Organization has made several policy recommendations to reduce salt intake and even implemented some policy approaches in several countries worldwide. Nevertheless, according to the European Food Safety Authority, approximately 75% of the salt we eat is already in the foods we buy. Thus, the best way to assure an effective reduction in salt consumption is to train our taste to the flavour of low-salt foods, although there is still a long way to go from awareness to action. The main goal of this chapter is to review the social and economic importance of salt throughout human history; its role in food preservation, food safety and food sensory evaluation; the impact of salt intake on human health; and the attempts to reduce or replace salt in food.

Keywords: sodium chloride, food safety, flavour, cardiovascular diseases, salt reduction, salt substitutes, history of salt

1. Introduction

Salt, also known as table salt or sodium chloride, is an ionic compound with the chemical formula NaCl, representing a 1:1 ratio of sodium and chloride ions.

The meekest of seasonings, table salt is commonly used as a condiment and food preservative. However, it was a precious commodity that played an important part in the development of the ancient world. For most of human history, salt was considered an extremely valuable commodity, as valuable as gold among ancient civilisations.

Therefore, salt was known as the "white gold", although several other commodities, such as sugar, cotton, marbles, ivory and water, also received that designation [1–9].

Salt was such an important commodity throughout world history that the word *salary* is linked to how wages were once paid in salt. Furthermore, the origins of the word *soldier* are also related to someone who was paid in salt [1].

In the centuries prior to the invention of electricity and refrigeration, salt was primarily used to preserve food. It was also a key ingredient in the curing of leather [1].

Salt has had the same economic importance as oil throughout most of human history. Therefore, in ancient times countries built their salt reserves before they went to war, so that enough food could be preserved for the forces being sent into battle [1].

Besides, salt was often taxed by nations and empires in the course of history. During the French Revolution, in regions where salt was scarce, it was worth up to 20 times more than in salt-producing regions. The death penalty was applied for smuggling salt! In India in 1930, the "salt tax" essentially made it illegal to sell or produce salt in competition with the established British monopoly on salt production. The quest for salt also played a crucial role in several battles in the American Civil War. For example, salt workers were exempt from being drafted into the army [1].

Currently, table salt, namely, sodium chloride (NaCl), is important in foods mainly due to its role on sensory appreciation, processing technology and preservation.

According to the European Food Safety Authority (EFSA), approximately 75% of the salt we eat is already in the foods we buy [10].

Nowadays, there is a growing concern with making foods nutritionally more balanced. Therefore, with the purpose of developing healthier foods, food reformulation is underway and comprises the modification of food composition by reducing or replacing ingredients, such as salt, fat and sugar [11]. In fact, recent studies have suggested that the biggest reductions in salt consumption were achieved by comprehensive strategies, such as food reformulation and media campaigns, associated to food policies, namely, regulations, taxation, mandatory reformulations and food labelling, while individual interventions on consumer education and dietary counselling have almost no effect [12, 13].

Despite the clear implications of excessive salt consumption for public health, moving from consumer awareness to action still seems to be a huge step to take [14]. Nevertheless, the adaptation to a less salty taste by consumers can be an important way to reduce salt content in food products [15–18]. Therefore, distinct strategies to implement salt reduction initiatives in different countries and among different target populations are needed [13].

2. The role of salt in food preservation

Salt is well-known for its role as flavouring agent and as food preservative both in industrial food processing and home cooking. Nevertheless, salt shows different technological properties in food production.

Dehydration was the earliest curing process, and, in order to preserve foods during dehydration, early civilizations salted foods to help desiccate them. Nowadays, this practice is still used.

Salt acts as a preservative by reducing the availability of water in foods, thereby depriving microorganisms from using available water as a nutrient [19, 20] and decreasing enzymatic activity [20]. The growth of pathogens and spoilage microorganisms is avoided or delayed in the presence of salt [20]. *Clostridium perfringens* and *Clostridium botulinum* are severely inhibited by salt, but *Staphylococcus aureus* and *Listeria monocytogenes* are relatively halotolerant [21].

Salt can be added to food products to assist in reducing and preventing microbial growth [22, 23]. This may be achieved either due to the bacteriostatic role of salt [24] or because of its ability to regulate enzyme activity [24], for example, through its influence on the growth of fermenting bacteria [20]. The main mechanisms responsible for the inhibition of microorganisms by salt include cellular plasmolysis, inhibited respiration, o-nitrophenyl- β -galactoside hydrolysis, glucose utilisation, prevention of substrate transport into the cells across cell membranes, limiting oxygen solubility and interference with enzymes [21]. Furthermore, sodium

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chloride may decrease enzymatic activity by denaturing enzymes, by reducing their catalytic activities and by altering their cofactors [25].

Salt can help to extend the shelf life of cured meat products, such as dry-cured ham, bacon and ham [26] or canned fish, namely, sardines, tuna, mackerel or anchovies, among others [27].

3. The technological role of salt in food production

Nowadays, the functional properties of salt in food processing and food production go well beyond taste. In fact, salt plays different technological roles in food production. Besides flavour, it has an important role also in safety and on textural properties. It also influences the growth of bacteria involved in fermentation processes [20].

Salt plays several main roles in the processing of different foods [23]:

Meat and meat products—It increases the water-holding capacity, tenderises raw meat and improves the binding of batters in processed meats.

Bread—It makes gluten more stable and less extensible and sticky, and it influences the fermentation rate.

Cheese—It modulates the microbiota, regulating the activity of starters and modifying enzyme activities, and it affects the cheese's body/texture by altering protein structure.

Canned foods—It can be used for cleaning fish, before canning.

Salt not only gives foods a "salty" flavour, but it can also enhance other flavours, such as aromatic notes. It balances sweetness and helps suppress flavours, such as bitterness.

Salt or better sodium chloride can also be a nutrient source for sodium, an essential nutrient needed by the body in small amounts.

Salt also plays a role as texture enhancer. It modifies the structure of proteins and modifies the interaction of proteins with other components, such as water and fat, which impacts the texture of foods. For example, if the proper amount of salt is added, cheese can have more body, meat can be juicier, and fish and breads can be firmer.

According to Akkerman et al. [28], low-salt cheeses were found to be less firm and more compressible. Moreover, Jian-Qiang et al. [29] studied mozzarella cheese and reported that salt content had influence on the meltability of no-salted immature cheeses.

Salt is also important as a binding and emulsifying agent. The new protein structure helps to hold the product together and helps to prevent moisture and fat loss. This is very important, for example, in processed meats.

NaCl has a main role in cheese manufacturing, namely, regulating the coagulant, the milk proteinase and microbial enzymes [30].

The gelling ability of food proteins is an important functional attribute for food manufacturing. The food industry uses different proteins to produce gels or gel-containing products which exhibit various rheological properties, appearance and gel point. Gelation is a basic process in the processing of various foods, namely, meat and other meat products, bread and bakery doughs, dairy products and fish products, among others. Salt, sugar and fat, included in the formulations of most food products, modify the properties gels, affecting the rheological and textural characteristics of foods [31].

3.1 Meat and meat products

Salt is undoubtedly the most ancient known ingredient, performing numerous functions in meat. Its addition to sausages' meat batters is mainly due to its activity in reducing water activity (a_W) , functioning as bacteriostatic, controlling the growth of

pathogenic microorganisms [32]. However, salt has many other effects of unquestionable interest. Salt promotes flavour and diminishes pH, which, due to the Donnan effect [33, 34], causes a decrease in the isoelectric point of proteins and consequently a higher water-holding ability.

Goutefongea [34] mentions that for salt concentrations of 10%, most saltsensitive bacterial forms are inhibited, while salt concentrations of 5% only inhibit anaerobic forms. More recently, due to demands related to consumer preferences, the salt concentrations used in meat products in the countries that are more aware of consumers' health does not exceed 3% [35]. However, in many other countries, such as Portugal, salt contents close to 6% are still found in traditional sausages, although there is a growing concern to reduce salt.

Salt is also added to some meat and meat products to influence water-holding capacity and give the products a moister texture [36]. Ionic strength, which is influenced by salt content, has a strong influence in gel formation. The use of approximately 2–3% sodium chloride in meat products is necessary to solubilise myofibrillar proteins [32, 36]. Therefore, salt improves texture.

Salt can also help to enhance flavour and colour [37, 38]. It can affect the final flavour through the control of the biochemical and enzymatic reactions throughout ripening [39].

3.2 Bread and bakery products

Salt is very important for the bakery industry because it can make dough texture a little stronger and tighter. Furthermore, it has an impact in the shelf life of baked goods, because it reduces water activity.

The main function of salt in bread is to bring out the good flavours and mask the off-flavours. Usage levels are usually around 2%. Legislation may vary from country to country because the intake of too much salt is considered as a health risk.

Salt helps slow down chemical reactions, including controlling the fermentation rate of yeast and dough development. Salt helps control yeast activity and strengthens the protein matrix that forms the crumb structure of the bread. It is, therefore, of utmost importance that the salt is completely dissolved in doughs. In addition to impacting flavour, salt also inhibits fermentation due to the osmotic pressure effect. Yeast cells will partially dehydrate due to the osmotic pressure. The effect of salt on fermentation can be used to control the fermentation process: salt can be added, for instance, to sponges to slow down the fermentation rate. Slowing down fermentation rate means that less sugars are metabolised into acids. The result is that the pH of the dough will be higher, and the crust colour will be darker. Salt also influences enzyme activity. Additionally, salt toughens the gluten; it has a conditioning effect on the dough. Weaker flours could be strengthened by adding salt. It can be used to improve the handling properties of the dough by reducing the stickiness. Even though it strengthens the gluten, it delays its formation during mixing. Salt lengthens the mixing time, so it is common to delay the addition of the salt to the mixer. Faster flour hydration is also seen with delayed salt. The reason why salt toughens the gluten must be sought in the fact that gluten is made of negatively charged proteins. Negatively charged molecules will repel and not attract each other. It is believed that the positive sodium ions (Na⁺) of salt play a role in bringing the protein molecules closer to each other. Finally, bread with no salt will also has a crust which is lighter in colour (given the same baking time and oven temperature). This can be explained as follows. Salt will slow down fermentation, so when there is no salt, the yeast activity will increase, i.e. the yeast will metabolise more sugar in the same amount of time. As a result, there will be less sugars left in the dough, and the pH of the dough will be lower (more acids will be formed). Sugars play (together

with proteins, moisture and heat) an important role in the Maillard reaction [40]. This reaction is a chemical and nonenzymatic browning reaction between an amino acid or a protein with a free amino group and a reducing sugar during the thermal processing and storage of foods [41]. In this reaction melanoidins are intermediate compounds, which are responsible for the resulting brown colour [40, 41]. However, the Maillard reaction is also influenced by pH: a higher pH will speed up the Maillard reaction. Therefore, in the case where the pH is lower and where there are less sugars left, the colour of the crust is lighter [42].

3.3 Other food products

Salt and milk proteins interact to provide an essential water-binding function. Furthermore, salt acts as a flavour enhancer and preservative in cheeses. In fact, salt has three major functions in cheese: it acts as a preservative, contributes directly to flavour and is a source of dietary sodium. Together with the desired pH, water activity and redox potential, salt assists in cheese preservation by minimising spoilage and preventing the growth of pathogens [43].

Seafood products or fishery and shellfish products include all wild or farmed seawater or freshwater fish, crustaceans, molluscs and surimi, whether fresh, frozen, cooked, salted, dried, smoked, fermented and marinated, as well as sushi [44, 45].

Fish and shellfish have been acknowledged for being high-protein, low-calorie foods rich in essential polyunsaturated fatty acids. They are also considered a valuable source of minerals and vitamins. However, they are quite perishable, mainly due to their intrinsic composition and habitat. This fact has contributed to the development and improvement of seafood preserving methods since ancient times [46].

Nowadays, salt is still used for seafood preservation, mainly in developing countries, although most salted fish and shellfish products are lightly salted, and for preservation other hurdles are used as well [46].

Salt favours lipid oxidation, accelerating rancidity and consequently affecting colour and flavour [47].

Salting is a process used in the preservation of several fish products, such as salted cod, sea bream, chub mackerel and smoked salmon, among others [48].

Cod (*Gadus morhua* L.) is a white fish traditionally commercialised as salted cod in Mediterranean countries. Different salting methods may be used for cod salting, giving the final product distinct characteristics [49].

Traditionally ripened herring is a protected product in Denmark. Beheaded herrings are put in plastic barrels with salt, sugar and some spices and kept for 36 months under refrigeration. This salting/ripening process is important mainly to produce a well-ripened product with a tender consistency and a pleasant taste and odour [50].

In the preparation of smoked fish products, such as smoked salmon, salt also plays an important role, since it decreases a_W [51].

The major five dietary sources of sodium in the USA are ready-to-eat (RTE) foods, namely, bread and rolls, meat products, pizza, poultry and soups [52].

Flavour enhancement is one of the primary functions of salt in processed and ready-to-eat foods. Moreover, salt is one of the tools used for preservation to control microbial growth.

In the processing of vegetable products, salt can be used as a preservative and/or softening agent but also in the fermentation process [48].

Salt plays a role in the flavour of cereals and other snack foods [53] and provides a texture and flavour enhancing function in crackers.

In sauces, such as mayonnaise, and dressings, salt is used for preservation purposes but also as a texturing and emulsifying agent [54].

Ready-to-eat shrimp, due to its processing, cooking in salted water, is also an RTE food with a high-salt, high-sodium content.

In canned foods, salt is added mainly to preserve the product.

4. Salt consumption and human health

Despite all the health problems associated to salt consumption, its excessive use is constantly growing. Ninety-five percent of the world's population in 2013 presented a mean salt intake between 6 and 12 g/day [55], and even nowadays the average of 9–12 g per day is pointed out by the World Health Organization (WHO). Many changes are necessary to reduce salt intake and achieve the necessary reduction in high blood pressure. All the WHO member states assumed the compromise of reducing by 30% the salt intake in their populations until 2025, estimating that 2.5 million deaths can be prevented with the adequate salt consumption [56].

In fact, hypertension, which constitutes one of the risk factors for cardiovascular disease, particularly coronary heart disease and stroke, is highly correlated with the excessive consumption of salt in the human diet [57]. On the other hand, hypertension has been associated with high intakes of sodium through the sodium chloride (NaCl) used in food. Still, sodium is important for distinct physiological functions and is essential for cellular homeostasis [58].

The WHO recommends that adults consume less than 5 g (just under a teaspoon) of salt per day [56].

This mineral is essential for human health to maintain plasma volume, regulating body water content and electrolyte balance, transmission of nerve impulses and normal cell function; however, its excess in human diet leads to high blood pressure. This problem is often correlated with high consumption of sugar and fat, besides salt.

However, a decrease in potassium intake and an unhealthy lifestyle are responsible for the increased numbers of noncommunicable diseases (NCDs). NCDs, also known as chronic diseases, result from a combination of genetic, physiological, environmental and behavioural factors and are generally prolonged in duration [12, 59]. The main types of NCDs are cardiovascular diseases (like heart attacks and strokes), cancers, chronic respiratory diseases (such as chronic obstructive pulmonary disease and asthma) and type 2 diabetes [59]. The "Global Action Plan for the Prevention and Control of Noncommunicable Diseases 2013–2020" include a 30% relative reduction in the intake of salt by 2025.

According to the WHO (2018), NCDs are the cause of 41 million deaths of people each year, being cardiovascular diseases the first cause of death. Cardiovascular disease is the leading cause of death in the USA [60].

The trials that studied the role of salt in the blood pressure begun with the studies in rats of Goldblatt [61]. Some years later, Kempner [62] stated for the first time that high salt could induce hypertension and low salt could lower blood pressure. This was followed by a huge number of clinical studies about sodium restriction to control blood pressure. The result of numerous trials along the years pointed out the importance of a diet with low income of salt to decrease blood pressure. Sacks et al. [63], in a meta-analysis of 31 trials, obtained a decrease of 5.0 mmHg of systolic and 2.7 mmHg diastolic blood pressure because of a decrease of 4 g of salt per day (which corresponds to sodium 75 mmol/day) in hypertensive patients.

However, nowadays, some researchers criticise these evidences referring that most trials evaluated high blood pressure, malnourished and mainly aged patients [64]. So, according to McCarron et al. [65] and Graudal and Jürgens [66], the

proposed salt daily intake for healthy people (normal blood pressure), and even the evidence of its negative role on blood pressure, should be reconsidered by health institutions and their policies.

Another aspect to be considered in human health is the necessity to evaluate jointly low sodium and high potassium intake, because high potassium consumption has a beneficial effect in preventing hypertension [67]. Potassium is present mainly in fruits, vegetables and unrefined foods and is essential for regulating fluid balance and controlling the electrical activity of the heart and other muscles and maintains normal cell function. Increased potassium intake reduced blood pressure, and it can mitigate the negative effects of elevated sodium consumption on blood pressure [68]. The WHO suggests a potassium intake of at least 3510 mg/day for adults.

The food reformulation, concerning modification in food composition with the development of healthier products, and at the same time consumer acceptance, is one strategy to achieve sodium reduction and a better intake of potassium in the human diet. Some countries, in Europe, published legislation for food reformulation by setting maximum levels for certain food components or by defining health targets. The National Salt Reduction Initiatives, developed in 2009, has the goal of reaching the maximum recommended intake of 5 g salt all over Europe.

Some recent findings indicate that human sodium intake is controlled by physiology and cannot be modified by public health policies [65].

Nevertheless, the reduction of the dietary salt intake remains a global public health priority [14].

5. Salt reduction and replacement studies

If the consumption of high levels of sodium (table salt contains 38.1% sodium) has been associated with hypertension, much effort has been spent on the complete or partial replacement of table salt (sodium chloride). It is not the salt as such, which is the culprit, but the sodium in the salt. Therefore, when discussing salt reduction, one must consider all sources of sodium.

Strategies on how to reduce salt content in food products without depreciating their quality have been proposed by several institutional and health-related organisations that recommend cooking with little or no added salt, valorising the natural taste of foods. The strategies may include, among others, seasoning with aromatic herbs, spices, lemon juice, wine and vinegar; use of marinades and garlic vines to season foods the day before; combining tasteless foods with foods of more intense flavour, such as onion, garlic, pepper and tomato; cooking with low amounts of water, to concentrate aroma and flavours; no addition of salt if the meal contains preprepared sauces, sausages or canned food; avoiding adding more salt while cooking; and not putting the salt shaker on the table.

Plain salt reduction studies are shown in Table 1.

Salt reduction can further be achieved in three main ways: replacement of sodium chloride by potassium chloride, addition of a flavour enhancer that enhances the salty taste even with lower salt contents and changing the physical structure of sodium chloride so that its crystals dissolve faster in the mouth, tasting saltier [47].

The most popular approach in reducing sodium chloride (NaCl) in the formulation of food products is to replace it with other chloride salts such as KCl, LiCl, CaCl₂ or MgCl₂ [36].

Potassium chloride (KCl) has been used as the main alternative to NaCl in salt replacement experiments, mostly because its antimicrobial effectiveness has been reported to be similar to that of NaCl [80].

Food product		Reference	
	Control (%)	Low salt (%)	
Traditional blood dry-cured sausages	6.0	3.0	[69]
"Catalão" and "Salsichão"	6.0	3.0	[70]
Hotdog sausages	3.6	2.8/2.0	[71]
Bacon	4.3	3.4/2.3	[71]
Ham	3.1	2.4/1.7	[71]
Salami	11.7	9.8/6.3	[71]
Bread	2.0	1.8/1.61/1.38	[72]
Cottage cheese cream	2.2	1.48/0.73	[73]
Pizza crust	1.09	1.02/0.99/0.91/0.84/0.76/0.51	[52]
Cheddar cheese	1.8–2.1	1.25/0.50	[74]
Prato cheese	1.68	1.23	[75]
Cooked ham	1.9	1.33/0.95/0.00	[76]
Soup	0.3/0.2/0.1	0.21/0.14/0.07	[77]
Dried fish	10	5	[78]
Durum wheat bread	2.0	1.5/1.0	[79]
"Painho de Portalegre"	6.0	3.0/2.0	This study

Table 1.

Salt reduction studies in different food products.

The effect on consumer acceptance or consumer perception of low-salt foods has been evaluated, and these studies should precede the development of new products by the food industry [81].

Table 2 summarises some recent studies on salt replacement, considering different food products.

As it can be seen from **Table 2**, there are numerous salt replacement studies on bread and meat products, whereas only a few on other foods.

Regarding bread and other bakery products, potassium chloride has a lower inhibiting effect on the yeast. Furthermore, proofing and mixing times are shorter. Moreover, potassium chloride is more difficult to dissolve in water than sodium chloride. Hence, it is important to choose "fine" potassium chloride and not a coarse grade. The undissolved grains will cause dark brown spots on the crust of the product. Still, KCl showed characteristics similar to NaCl in baked products. However, other salt replacers, such as magnesium chloride, ammonium chloride, magnesium sulphate or calcium chloride, have limited application due to their more unpleasant flavour [97].

Aromatic and medicinal plants (AMP) can also be used as flavouring agents, giving a tastier flavour to foods and thus enabling salt reduction [98]. Herbs or AMP, namely, oregano, basil, marjoram, thyme and bay leaf, added to fresh soups, reduced the need for salt intake when the perceived herb flavour increased [87]. Spices have also been added to dried fish goldstripe sardinella (*Sardinella gibbosa*) to reduce the amount of added salt [78].

Salicornia sp. is a wild food plant with long history of human consumption that has been used in traditional vegetable mixtures in Italy [99] and is known for its salty taste and high nutritional values [100].

Food product	Salt substitute	Reference
Cooked ham	KCl	[76]
Dry-fermented sausages	KCl	[82]
Fermented sausages	KCl/potassium lactate/glycine	[83]
Dry-cured pork loin	KCl/potassium lactate/glycine	[83]
Dry-fermented sausages	Calcium ascorbate	[84]
Pork sausage patties	KCl	[85]
Dry-fermented sausages	KCl/CaCl ₂	[86]
Fresh and canned soups	Herbs	[87]
Bread	KCl/yeast extract	[88]
Bread	CaCl ₂ /CaCO ₃	[89]
Wheat bread	KCl/MgCl ₂ /CaCl ₂	[90]
Brown bread	Calcium carbonate/MgSO ₄ /MgCl ₂ /KCl	[91]
Cheddar-style cheese	KCl/MgCl ₂ /CaCl ₂	[92]
Mozzarella cheese	KCl	[93]
Pizza crust	KCl	[52]
White bread	CaCl ₂ /MgCl ₂ /KCl/MgSO ₄	[94]
Fermented sausages	KCl	[95]
Dry-cured loins	KCl	[96]
Slow-fermented sausages	KCl	[15]
Cooked ham	KCl	[76]

Table 2.

Salt replacement studies in different food products.

5.1 Meat and meat products

Several studies have reported the reduction of salt content in meat products and its partial replacement with other salts, such as potassium chloride (KCl), magnesium chloride (MgCl), lithium chloride (LiCl), calcium chloride (CaCl₂) and phosphates [101].

However, concerning dry-cured meat sausages, it is more difficult to develop low-salt traditional products. Sodium chloride has a determinant effect both in flavour as in the microbiological stability of sausages.

Gou et al. [83] used potassium chloride, potassium lactate and glycerine as partial substitutes for sodium chloride in the formulation of fermented sausages. However, major defects were found regarding aroma and flavour when these salts replaced more 40% of the sodium chloride content. These authors also found changes in texture when the NaCl was replaced by potassium lactate at levels above 30% or by glycine at levels 50%.

Ibáñez et al. [82] detected the development of nitrosamines and the heterofermentative activity of carbohydrates by starter cultures were favoured by a mixture of 1.37% NaCl and 0.92% KCl, when compared to the same sausages manufactured with 2.73% NaCl.

Other studies have shown a sensory depreciation in sausages with 1% NaCl, 0.55% KCl, 0.23% MgCl₂ and 0.46% CaCl₂, when compared to sausages with 2.6% NaCl [84]. A significant reduction in the sodium content of Spanish sausages was

Microbiological groups (cfu/g)	Salt content (% NaCl)	
	2%	3%
Total mesophiles	7.44	7.93
Total psychrotrophic microorganisms	7.25	7.85
Yeasts	2.60	4.28
Moulds	n.d.	n.d.
Gram-positive, catalase-positive cocci (GCC+)	6.59	5.38
Lactic acid bacteria (LAB)	8.46	8.41
Enterobacteria	3.21	2.90
Enterococci	5.86	5.66
Spores of aerobic bacteria*	3.11	3.98

Table 3.

Microbiological analyses of traditional Portuguese dry-fermented sausages (Painho de Portalegre) with low-salt content.

achieved by the partial replacement of NaCl by different percentages of calcium ascorbate [86]. However, these sausages showed worse results for colour and texture when compared with control sausages.

Regarding microbiological parameters, no unwanted changes were noticed with the replacements of NaCl by other salts, in all the above-mentioned studies. From a sensory point of view, the major advantage of these sausages seems to be the insufficient salty flavour.

In a study regarding the microbiological, physicochemical, biochemical and sensory characteristics of traditional sausages from Alentejo, Portugal (*Painho de Portalegre*), instead of replacing NaCl, the authors reduced its content to 3% in the final product. The influence of salt content (2 or 3% NaCl in the final product) on the microbiota and the rheological and sensory properties of sausages were evaluated, and the results are shown in **Table 3**.

The number of mesophiles did not vary significantly, although the sausages with 3% NaCl have slightly higher counts. These results seem to indicate that the natural microbiota of these sausages is characteristically halotolerant. This is even more evident for yeasts. On the other hand, the counts of enterobacteria and enterococci are higher in 2% NaCl sausages. Considering that these microbiological groups are associated with the hygiene conditions of the manufacturing process, the bacteriostatic role of salt was beneficial. As for the technological microbiota [102, 103], the lactic acid bacteria, still present in high numbers in the final product, which is characteristic in this kind of sausage, almost do not vary with the sodium chloride concentration. Interestingly, Gram-positive, catalase-positive cocci (GCC+) show higher counts in the 2% sausages, although they usually grow well in the presence of salt [104]. The counts of all other microbial groups did not vary with salt content.

Regarding sensory analysis (**Table 4**), sausages with 2% NaCl showed higher colour intensity values, but 3% NaCl sausages were tender (confirmed by the rheological tests), more succulent and with higher flavour intensity. The results obtained for these two last attributes may be because salt stimulates salivation and potentiates the flavour of foods. Concerning global appreciation, there was a slight preference for the sausages with less salt.

Generally, the microbiota of these sausages did not vary with salt content. Furthermore, concerning sensory analysis, no significant differences were observed

Sensory attributes	Salt content (% NaCl)		
	2%	3%	
Colour intensity	75.6 ± 9.3	61.8 ± 18.2	
Aroma intensity	69.4 ± 12.3	65.0 ± 8.8	
Tenderness	65.0 ± 16.6	74.6 ± 14.5	
Fibrousness	31.4 ± 22.1	29.8 ± 19.9	
Succulence	66.75 ± 9.7	70.0 ± 10.0	
Flavour intensity	67.6 ± 10.5	72.2 ± 5.3	
Off-flavours	5.2 ± 8.4	8.0 ± 13.0	
Salt intensity	56.0 ± 9.0	64.0 ± 11.4	
Global appreciation	71.2 ± 11.2	69.0 ± 6.5	
ta are expressed as means ± standard deviation	on.		

Table 4

Sensory analysis of traditional Portuguese dry-fermented sausages (Painho de Portalegre) with low-salt content.

for any of the studied attributes. Furthermore, the rheological analysis showed no influence of salt content in the studied attributes.

Furthermore, the production of *Painho de Portalegre* is characterised by a different formulation regarding salt content. These may significantly influence the qualitative and quantitative formation of biogenic amines, since they modulate the microbiota throughout the manufacturing process. Thus, regarding the profile in biogenic amines, differences were detected between the two salt concentrations.

In another study with *Painho de Portalegre*, the effect of salt in the profile of biogenic amines was evaluated. Differences were observed between the two salt concentrations in the final product, 3 and 6% NaCl (data not shown). The content in biogenic amines, mainly cadaverine, putrescine, tyramine and β -phenylethylamine, was severely reduced in 6% NaCl sausages throughout the curing period.

Several other studies on traditional Portuguese sausages have shown the neutral or positive effect of salt reduction on these products.

Salt reduction does not negatively affect the quality and acceptability of sausages [105].

Sensory evaluations revealed that despite the less intense aroma, products with 3% salt had a more balanced salt perception. Our results suggest that salt content may be reduced to 50% in dry-cured products, with the obvious health-related advantages [70].

Low-salt sausages were clearly preferred by panellists [69].

The reduction in salt content from 6 to 2% in large calibre pork sausages did not compromise safety nor depreciate the sensory acceptability of the products [106].

Coutron-Gambotti et al. [107] studied the effect of salt reduction on the lipidic composition and sensory attributes of dry-cured ham and observed a reduction in the number of autoxidation processes and a consequent improvement of aroma and flavour. Regarding rheological analysis, salt content did not significantly influence the textural characteristics of the sausages, namely, hardness, cohesiveness, elasticity, gumminess, chewiness and shear force.

Regarding consumer acceptance studies, low-salt small calibre fermented sausages with a NaCl/KCl 50:50 ratio were found to be acceptable for consumers [95]. Moreover, dry-cured loins also with a 50:50 ratio NaCl/KCl obtained the highest scores in sensory evaluation by a trained panel [96].

Salt in the Earth

Tamm and co-workers [76] produced low-salt cooked hams (30% reduction) without significant differences in water binding and texture compared to regularsalt hams, by combining the use of a high isostatic pressure treatment with the partial replacement of NaCl by KCl.

5.2 Bread and bakery products

Bread is a major contributor to sodium intake. Therefore, a reduction in the salt content of bread would cause a great impact on global health.

Recently, there has been quite some pressure on the bakery sector to reduce the salt content in bread, cakes and muffins, among others. Potassium chloride has been regarded as an acceptable substitute for sodium chloride as it has basically the same rheological effects on the dough. However, if sodium chloride is replaced by the same amount of potassium chloride, the bread will have a bitter aftertaste. This is only a problem in bread; it does not occur in products such as muffins or cakes, because this aftertaste mostly disappears after 2 or 3 days and it can be masked using eggs and butter.

Reduction of salt in bread involves changes in quality characteristics, such as flavour, shelf life and texture. Besides, the manufacturing process is affected by changes in dough stickiness [40]. The replacement of NaCl by KCl does not have any significant processing disadvantages but has a negative impact on flavour [40].

Several studies have evaluated the acceptable replacement levels of NaCl by KCl in bread [108, 109].

5.3 Other food products

Strategies for reducing "salt" in cheese include mainly the reduction of table salt (NaCl) and its replacement by potassium chloride (KCl). However, these strategies present many challenges, such as adverse effects on flavour, microbiological stability and functional properties of the final product. When salt content is simply reduced in natural cheese, proteolysis, water activity, acidity and bitterness all increase, while hardness decreases. In addition, irregular fermentations could occur which may alter the desired characteristic taste of the cheese, namely, the development of a bitter unacceptable flavour.

In cheddar cheese, which has been extensively studied with respect to salt reduction, analysis showed that reducing NaCl resulted in an unpleasant aftertaste and bitterness. Within a range of 0.5–3% salt, at salt levels below 1.5% compared to higher levels of 1.8–3%, an increase in the growth of undesired non-starter bacteria occurred that caused bitter flavours due to excessive proteolysis [74].

The reduction and/or replacement of sodium chloride (NaCl) by potassium chloride (KCl) in cheese is a difficult task that may affect the global desired quality of the cheese. It depends, among other factors, on the type of cheese. The different manufacturing processes make it easier to reduce or replace table salt in processed cheeses than in natural or soft cheeses [110].

The reduction of salt levels in cheese can be done over a period of time, to prevent the consumer from detecting organoleptic changes [111].

NaCl reduction in cottage cheese cream dressing is possible from a mechanical or rheological point of view, without significantly changing the sensory acceptability of the product [73].

Processed foods, namely, those with a high salt content for preservation, such as pickles, smoked foods, concentrated broths and meat-based food, namely, patties, croquettes, sausages and ham, canned seafood, fish and meat, dried or

salted codfish, crackers and industrial sauces, are responsible for most of the salt consumed. Therefore, when cooking and eating at home, consumers should avoid these foods.

Potential effect of salt reduction in processed foods has been reviewed [112].

Pizza is a major contributor to the daily sodium intake [52]. Mueller and coworkers prepared pizza crusts with reduced sodium contents of up to 25%, without depreciating their sensory evaluation [52].

Ready-to-eat foods to take away or served in restaurants also contribute immensely to the salt intake of the modern consumer. Ahuja and colleagues [60] reviewed the subject and emphasised the importance of public health efforts together with food manufacturers and restaurants to reduce the sodium levels in prepared meals.

6. World policy, particularly in the European Union

The WHO has made several policy recommendations to reduce salt intake, restrict or eliminate choice, guide choice through (dis)incentives, enable or guide choice through changing default (reformulation and marketing), restrict or eliminate choice, provide information (public health campaigns and labelling) and monitor. These may be combined to effectively reduce salt consumption [113].

Likewise, some policy approaches have already been implemented, which mainly pursue the objectives: to provide information, to make the healthy option available or to provide financial (dis)incentives related to salt consumption [113]. Several governments from countries around the world have adopted national salt reduction strategies, which range from legal obligations, such as the limit of salt content in bread, to intended actions involving the food industry, mainly regarding reformulating of food products [13].

Food product	Country	Salt level (%)	Reference
Bread	Austria	15% reduction	[114]
Bread	Belgium	<2%	[114]
Bread	Bulgaria	<1.2%	[115]
White cheese in brine	Bulgaria	<3.5 ± 0.5%	[115]
Yellow cheese "Kashkaval"	Bulgaria	1.8–3.0%	[115]
Durable boiled smoked sausage	Bulgaria	≤3.5%	[115]
"Lutenica"*	Bulgaria	≤1.7%	[115]
Bread	Croatia	30% reduction in added salt	[114]
Bread	Finland	Low-salt threshold: 0.7%	[114]
Sausages	Finland	Low-salt threshold: 1.2%	[114]
Cheese	Finland	Low-salt threshold: 0.7%	[114]
Fish products	Finland	Low-salt threshold: 1%	[114]
Breakfast cereals	Finland	Low-salt threshold: 1%	[114]
Butter	Finland	Low-salt threshold: 1%	[114]
Soups	Finland	Low-salt threshold: 0.5%	[114]
Sauces	Finland	Low-salt threshold: 0.5%	[114]
Ready-made dishes	Finland	Low-salt threshold: 0.5%	[114]
Crisp bread	Finland	Low-salt threshold: 1.2%	[114]

Food product	Country	Salt level (%)	Referen
Bread products	Finland	Heart symbol: <0.28% sodium	[114]
Bread	Greece	<1.5%	[115]
Tomato juice	Greece	<1%	[115]
Concentrated tomato puree paste	Greece	<4%	[115]
Biscuits	Greece	<0.5% sodium	[115]
Bread	Hungary	16% reduction	[114]
Various food products	Ireland	"Reduced salt" status: >25% reduction	[114]
Bread and bakery	Italy	10–15% reduction	[114]
Food served in schools	Latvia	<1.25 g salt/100 g	[114]
Food served to children	Lithuania	<0.4 mg sodium/100 g	[114]
Bread	Netherlands	<1.8%	[114]
Bread	Portugal	<1.4%	[114]
Food served in schools	Romania	<1.5%	[115]
Food served in schools	Romania	<0.6% sodium	[115]
Bread	Spain	26.4% reduction	[114]
Bread	UK	<1.0–1.2%	[115]
Bread	UK	<0.6% sodium	[116]
Bread	Turkey	<1.4%	[114]
Bread	Argentina	<0.6% sodium	[116]
Bread	Brazil	<0.6% sodium	[116]
Bread	Canada	<0.6% sodium	[116]
Bread	Chile	<0.6% sodium	[116]
Soup	Argentina	<0.36% sodium	[116]
Soup	Brazil	<0.36% sodium	[116]
Soup	Canada	<0.36% sodium	[116]
Breakfast cereals	Canada	<0.63% sodium	[116]
Breakfast cereals	Chile	<0.63% sodium	[116]
Cooked, uncooked, processed meats/sausages	Argentina	<1.21% sodium	[116]
Cooked, uncooked, processed meats/sausages	Brazil	<1.21% sodium	[116]
Cooked, uncooked, processed meats/sausages	Canada	<1.21% sodium	[116]
Dry-cured meats and meats conserved at RT	Argentina	<1.9% sodium	[116]
Dry-cured meats and meats conserved at RT	Brazil	<1.9% sodium	[116]
Dry-cured meats and meats conserved at RT	Canada	<1.9% sodium	[116]
Mayonnaise	Brazil	<1.05% sodium	[116]
Mayonnaise	Canada	<1.05% sodium	[116]

Food product	Country	Salt level (%)	Reference
Mayonnaise	Chile	<1.05% sodium	[116]
Cookies and sweet biscuits	Argentina	<0.485% sodium	[116]
Cookies and sweet biscuits	Brazil	<0.485% sodium	[116]
Cookies and sweet biscuits	Canada	<0.485% sodium	[116]
Cookies and sweet biscuits	UK	<0.485% sodium	[116]
"Mozzarella" cheese	Brazil	<0.559% sodium	[117]
Various food products	USA	"Healthy claim": <1.1 mg sodium/kcal	[60]

Table 5.

Policy on salt reduction per food product in different countries.

In 2013, the salt reduction initiatives in the WHO European Region have been mapped and described by country [114]; however, the progression has been slow, and salt intake in most WHO European Region countries is far above the suggested amount [18]. Some countries adopted initiatives to reduce the total amount of salt consumed (maximum daily intake), others the amount of sodium, but only a few legislated the amount of salt added to food products and mainly to bread [60, 114–117].

In Portugal, an agreement was signed on May 2, 2019, between the *General Directorate of Health*, a central department of the Ministry of Health, and seven food industry and food distribution associations, to reduce the content in salt, sugar and *trans* fats in over 2000 food products, for a healthier diet [118].

In a study conducted in the USA with processed and restaurant foods, more than half of the analysed foods exceeded the US Food and Drug Administration's (FDA) sodium limit for using the claim "healthy" [60]. This "healthy" claim reports to the Healthy Eating Index-2010 [119] and to an optimal sodium level below 1.1 mg/kcal.

Systematic reviews on salt reduction initiatives in different countries around the world have been published previously [12, 13].

A non-exhaustive summary of the current national initiatives per food product comparing policies between different countries, mainly of the European Union, is shown in **Table 5**.

7. Conclusions

Salt (sodium chloride) has played different but very important roles throughout human history. It has been an important product, firstly for its action in food preservation and for its role as flavour enhancer. More recently, the effect of salt on some food components, namely, proteins, has also been recognised. In fact, salt modifies the structure of proteins and their interaction with other food components, which has consequences on the technological properties of those food products (meat and meat products, bread and other bakery products, cheese and other dairy products and canned fish products, among others). Regarding the technological role of salt, it also has an evident effect on microbial modulation, which is particularly important in fermented products and regulating the enzymatic activity. This fundamental role of salt has been an obstacle to the reduction of its consumption, the latter being related to the occurrence of consumer health problems, namely, cardiovascular diseases. Adapting ourselves and training our taste to the flavour of low-salt food is undoubtedly the best way to assure the reduction of salt consumption. For the above-stated reasons, the WHO recommends a daily salt intake of 5 g per day for adults. Following these recommendations, several countries have implemented distinct measures to reduce the consumption of salt in different food products. Furthermore, numerous studies have been performed to find adequate alternatives to replace salt.

Nevertheless, some recent studies have unravelled that the negative effect of salt in human health has been systematically supported by trials, whose target groups were more susceptible to salt intake, such as hypertense, malnourished or elderly people. Therefore, new studies with healthy groups are needed. Moreover, there are recent studies that suggest the need to evaluate the intake of sodium and potassium comparatively, because potassium seems to have a beneficial effect in preventing hypertension, one of the predispositions for cardiovascular diseases. To cite Chris Kresser [120], it is important to question ourselves and "shake up the salt myth".

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Conflict of interest

The authors declare that they have no conflict of interest.

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Chapter 3

Systematic Reduction of Excessive Salt Intake

Boris Kovač and Urška Blaznik

Abstract

This chapter emphasizes the health outcomes connected with excessive salt consumption and focuses on possibilities to reduce dietary salt intake. The biggest reductions in salt consumption in the population could be achieved by comprehensive strategies involving population-wide policies (regulation, mandatory reformulation and food labelling). Salt reduction policies include the baseline identification of population's salt consumption and major sources of salt in the diet, reformulation of a set number of products available on the market and increased awareness and knowledge on salt reduction at an individual level, creating an environment for salt reduction and the promotion of 'healthy food'. Innovative reformulation by food industry, therefore, has the potential to contribute substantially. Flavours of processed foods could be improved by partially replacing salt with salt substitutes and flavour enhancers. One of the approaches of salt reduction is 'gradual reduction without the consumer's knowledge', which refers to the observation that people in general are unable to differentiate between two substances in which the difference in salt content is low. It is suggested that increased knowledge and appropriate promotion of healthy food and healthy dietary habits, especially in early childhood in kindergartens, schools and at home, are the most promising measures for salt reduction.

Keywords: excessive salt intake, cardiac diseases, products reformulation, salt reduction policies, adequate dietary habits, WHO

1. Introduction

Salt is the primary source of sodium, and high salt intake is associated with hypertension and increased risk of heart diseases and stroke [1–4]. It is well known that high salt intake is the major cause of raised blood pressure and accordingly leads to cardiovascular diseases. Well-conducted cohort studies and few intervention trials showed that a lower salt consumption is connected with lower risk of cardiovascular events [4–6]. Studies [7–9] also suggest a link between excessive salt intake and gastric cancer and type 1 diabetes. A modest reduction in salt intake has a significant effect on blood pressure both in individuals with raised blood pressure and in those with normal blood pressure. These findings provide additional support for a reduction in population salt intake. Furthermore, the meta-analysis [5] shows a dose-response correlation between the reduction in salt intake and the drop in blood pressure. Sodium reduction results in a decrease in blood pressure in normotensives; decrease in hypertension; a significant increase in plasma renin, plasma aldosterone level, plasma adrenaline and plasma noradrenaline; an increase in LDL cholesterol; and an increase in triglyceride [10]. Systematic study and meta-analysis

of prospective studies [8, 9] show that dietary salt intake is directly connected with the risk of gastric cancer in prospective population studies—the bigger the consumption of salt, the greater the risk of cancer. An overview study suggested [9] that dietary salt restriction as part of medical nutritional therapy would be useful in patients with type 1 diabetes, while the association between dietary salt intake and health status in patients with type 2 diabetes are confusing. Recently, some studies have shown that high salt intake is correlated with an increased risk for obesity [11, 12]. One of the reasons for this correlation could be the fact that high salt intake stimulates thirst and increases fluid intake and therefore increases the consumption of sugar-containing beverages [13]. The connection between salt intake and obesity may also be partially caused by excessive consumption of processed food that is high in both calories and salt. However, more and more evidence suggest that excessive salt intake is a potential risk factor for obesity regardless of energy intake [11, 13].

It is also recommended to reduce sodium/salt intake in children in order to control blood pressure. These recommendations recognise that salt reduction is compatible with salt iodization, which is considered as a key public health measure for assuring adequate iodine intake in iodine-deficient countries. Sufficient dietary intake of iodine is crucial for preventing iodine-deficiency disorders such as goitre, neurocognitive impairment, hyperthyroidism and hypothyroidism [14, 15]. Iodized salt used for cooking and at the table in households continues to be the major source of iodine in many countries around the world [15]. Dietary salt reduction should be complementary also with the increased level of potassium consumption. Epidemiological studies suggest that for determining the relation between blood pressure and cardiovascular disease risks, the optimal sodium-to-potassium ratio may be more important than individual levels of sodium and potassium [16, 17]. Potassium is commonly found in a variety of unrefined foods, especially fruits and vegetables; food processing reduces the amount of potassium in many food products, and a diet high in processed foods and low in fresh fruits and vegetables is often lacking in potassium. On the other hand, it is important to stress that excessive potassium intake could be reached by consuming some salt replacers. Consumed in excess, potassium may be harmful for some people with kidney problems.

2. Dietary salt reduction policies

Increasing production of processed food, rapid urbanisation, and changing lifestyles are transforming dietary patterns. Highly processed foods are more and more available and are becoming more affordable. People around the world are consuming more energy-dense foods that are high in saturated fats, sugars, and salt. The evidence supporting global actions for a moderate reduction in salt consumption in order to prevent cardiovascular diseases are strong as recently demonstrated in a scientific statement from the European Salt Action Network (E.S.A.N.) by Cappucio et al. [18].

The overall goal of the global salt reduction push is a 30% relative reduction in average population salt intake towards the World Health Organisation (WHO)— recommended level which is less than 5 g per day for adults [19]. This is the only a nutrition-specific target and a core component of the Global Action Plan for the prevention and control of noncommunicable diseases 2013–2020 [20], which aims to achieve a 25% reduction in premature mortality from avoidable noncommunicable diseases (NCDs) by 2025.

The number of countries that are taking action on salt reduction is increasing, but further action is critical to reduce the health consequences of consuming too much salt, particularly in low- and middle-income countries where the risk of

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death from high blood pressure is more than double that in high-income countries [21]. The WHO has been promoting the use of the SHAKE tools to assist Member states technically [22]. Strategies for salt reduction will differ in each setting, but it is likely that the main element of the strategy will be a combination of actions targeting consumers, industry, and government in addition to strong leadership and political commitment [23].

Important elements in interventions to reduce salt intake in the population, set out by the SHAKE package [22], are:

- government policies—including appropriate fiscal policies and regulations to ensure that food manufacturers and retailers produce healthier foods or make healthy products available and affordable;
- working with the private sector to improve the availability and accessibility of low salt products;
- consumer awareness and empowerment of populations through social marketing and mobilisation to raise awareness of the need to reduce salt intake consumption;
- creating an enabling environment for salt reduction through local policy interventions and the promotion of 'healthy food' settings such as schools, workplaces, communities and cities; and
- monitoring of population salt intake, sources of salt in the diet and consumer knowledge, attitudes and behaviours relating to salt to inform policy decisions.

Recent systematic review of salt reduction interventions by Hyseni et al. [24] introduced 'effectiveness hierarchy' of interventions (**Figure 1**) that suggested the biggest reductions in salt consumption in the population could be achieved by comprehensive strategies involving 'upstream' population-wide policies (regulation, mandatory reformulation and food labelling). This is particularly emphasized in middle-to-low income countries, as this is the only way to successfully change the food environment and thereby achieve a reduced salt intake in the population [25, 26]. 'Downstream' individually-based interventions appeared relatively weak

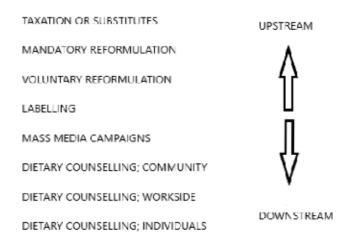


Figure 1. Interventions classified on the upstream/downstream continuum; adapted from [24]. (e.g. dietary counselling for individuals, media campaigns in isolation). Effects of population-wide policies size from 4 g/day in Finland in Japan, 3 g/day in Turkey and 1.3 g/day in the UK. It has been estimated that mandatory reformulation alone could achieve only a reduction of approximately 1.4 g/day.

Different countries are currently at different stages in the development and/or implementation of salt reduction initiatives. In the United Kingdom, the Scientific Advisory Committee on Nutrition published its Salt and Health report already in 2003, which recommended that salt intake should be reduced to no more than 6 g/ day for adults. Government in 2006, challenging the food industry to reduce salt in everyday foods, first introduced salt targets. Salt reduction has been ongoing for more than a decade, and many food categories have shown much improvement, with some products like breakfast cereals now 40% less salty than a decade ago [27]. EU salt reduction activities within E.S.A.N. consider development and alignment of product-specific targets, expanding methods of monitoring food composition, modelling the health impact of efforts and enhancing the knowledge about consumer attitudes, knowledge and behaviours [28]. In the USA, salt reduction work spans across federal, state, and local government agencies. Voluntary efforts by the food industry have been unsuccessful in lowering overall salt intake; further changes in the food supply are needed to bring salt intake within recommended levels [29]. The Australian Federal Government launched Food and Health Dialogue (FHD) in 2010. The focus of the FHD has been on voluntary reformulation of foods, primarily through salt reduction targets [30]. Later in 2015, the Victorian Salt Reduction Partnership (VicSalt Partnership) started bringing together health and research organisations to develop an action plan for salt reduction interventions at a state level [31]. In conclusion, salt reduction activities are currently being implemented through a variety of different programs, but additional efforts and more robust national monitoring mechanisms are required to ensure that countries would achieve the proposed 30% reduction in salt intake within the next decade.

More than 75% of dietary salt comes from the processed foods [32]. Some of the highest contributors of salt to our diets include condiments including table salt, followed by cereals and cereal products (including bread and some types of pizza), meat and meat products (including processed meat such as bacon, ham and sausages) and dairy products (including cheese) [33–35]. Product reformulation by food industry has, therefore, the potential to contribute substantially. However, in order to reduce intakes successfully, consumers need to be encouraged to reduce their salt intake by making healthier food choices and limiting salt used in cooking and added at the table [36–38].

Consumer food selection can be guided by effective and accurate labelling and marketing of food. In salt reduction, the purpose of labelling is to lead food selection towards healthier choices that contain less salt. Nutrition labelling, particularly front-of-pack labelling, may also encourage reformulation of food products. There are a variety of both voluntary and mandatory nutrition labelling systems in use around the world, most commonly applied to pre-packaged food and beverage products. While nutrient declarations (including salt) have to be displayed on all pre-packaged foods, 'front-of-pack' labelling can be used as an additional tool by displaying easily understood information about the nutrient quality of food products (nutrition claims) [39]. Consumers are appealed in salt reduction campaigns to regularly check front-of-pack labels for salt content or scan the barcode using free food scanner apps.

Salt should be seen in the crowded nutrition space, particularly in view of the current consumer concerns around other nutrients, like sugar. Using targeted messaging to highlight the harmful impact of salt on health outcomes was identified as a motivator for behavioural change. For example, the UK government used the message 'Salt Kills' in the first stage of their campaign [37]. In Finland, high-salt

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warning labels were placed on high salt foods from 1993, resulting in both a decrease in salt intake and reformulation of foods to reduce salt [40]. With reducing salt in the food products, the maintaining consumer acceptance of the products is a challenge. Consumer's perception of salt-reduced foods is of crucial importance for their market success.

Choosing products with lower salt content is one of the possibilities; there are still improvements in eating habits at home. Salt consumption can be reduced by not adding salt during the preparation of food, not having a saltshaker on the table and limiting the consumption of salty snacks.

The knowledge, attitudes and behaviours related to dietary salt intake in highincome countries are low. The same is true for the middle- and low-income countries [41, 42]. Consumers are aware of the health outcomes of a high salt intake, but the fundamental knowledge regarding recommended dietary intake, sources in food and the relationship between salt and sodium is lacking. If in countries with higher income we note that knowledge and more healthy behaviour increase with increasing education, some studies from countries with medium or low income these correlations are not noticed. Their awareness is low regardless of the level of education [42, 43]. Raising awareness of the health impact of salt consumption and the major sources of salt in diets will help to influence consumer behaviour. Strategies that are targeted at behavioural change can then be used to empower people to improve their diets and increase demand for lower-salt food products [44, 45].

Education and communication strategies can lead to changes in social norms relating to salt consumption, increased demand for healthier and lower-salt products, and improvements in overall health for individuals and communities. Economic evaluations clearly show that health education strategies are found to be cost-effective in low- and middle-income countries [46]. Improved health literacy might influence nutritional habits and well-being. However, empirical research on this topic is limited and connection between food and health literacy and diet still needs to be established [47].

Traditionally, dietary recommendations have been set at the average population level. To affect behaviours relating to salt reduction, mass media campaigns are widely used. Typical campaigns place messages not only in media with large audiences such as television or radio, but also on billboards, posters, magazines and newspapers. However, current research is increasingly showing that the risks, benefits and nutritional requirements strongly vary between different population groups depending on their characteristics. Salt reduction campaigns should therefore use innovative social platforms such as the internet, mobile phones, and personal digital assistants to deliver messages to individual's social network [47]. Salt reduction campaigns, designed as mass media or at the individual level, should be properly planned and preferably be multiyear programmes rather than one-off initiatives.

Individuals, who already have elevated blood pressure, and any of the cardiovascular diseases, are advised to decrease salt intake from food [10], so they can follow all salt reduction strategies. A special sub-group of people who have a disease or who are taking medication that can lead to hyponatremia or acute build-up of body water or need a controlled diet may have specific links between sodium intake and health outcomes, and therefore, they require physician-supervised diet [15].

3. Possibilities of salt reduction in food products by reformulation

The experiences of the countries that have introduced salt intake reduction measures in the diet of the population show that it is necessary to systematically and gradually reduce the consumption of salt. Salt (NaCl) affects different properties of food: flavour, preservation and texture. All this happens to different extents depending on the type of food product. Reduction of salt in food products is relatively simple if the salt is used only for a sensory aspect. As some salt is needed in foods for functional reasons, engagement with the food industry is an essential first step to understanding the feasibility of reductions in specific foods as well as to encourage reformulation efforts [22]. Lack of salt in a food product can lead for example to unstable meat emulsion products or bread that stales quickly and has frail texture and lighter crust colour. One of the strategies when dealing with texture issues with low salt content is to find solutions that have ionic strength similar as salt. Salt reduction, therefore, means balancing between taste and side effects. When preparing, for example, meat products, salt is not added only to make food tasteful, the salt also extends the shelf life of dried products. NaCl is used as an essential ingredient in processed meat because of its antimicrobial effect, the ability to enrich the flavour of the product and its functional ability to dissolve myofibrillar proteins, which increases the adhesion and cohesiveness of meat particles in processed meat products [48]. The antimicrobial effect of salt is based on its ability to reduce water activity. Inhibition of the growth of microorganisms is in correlation with the amount of salt present in the aqueous phase of food. Adding sodium ions to the meat causes water loss through the semipermeable membrane of bacteria. Water loss is an osmotic shock that can cause bacterial cell death or cause serious injury, resulting in a significant reduction in bacterial activity [48]. Salt can also affect oxygen solubility, reduce enzymatic activity, or consume energy to exclude sodium ions from cells, which can reduce the growth rate of microorganisms [48].

However, taste and microbial stabilisation are not the only reasons for use of high levels of sodium/salt in food. The level of salt is generally kept high due to the additional practical roles it provides. The presence of salt in meat products solubilises meat proteins, activates extraction of proteins, enhances hydration, water holding capacity and formation of heat-stable emulsions. Salt increases cooking yield and juiciness of the product [49, 50]. The consequences of salt reduction could affect shelf life and quality of processed meat products.

Current approaches of salt intake reduction include decreasing of salt content by stealth, using salt alternatives or using flavour enhancers. Reduction by stealth consists of a step-by-step salt reduction over a longer period of time. The major outcome is that modification in saltiness is not detected by consumers. The result should be acceptable saltiness of the product without apparent organoleptic changes determined by consumers [51, 52]. This strategy shows some weaknesses: it is time-consuming and, in addition, to reach everybody, it needs to be applied on a wide scale. All producers should be uncompromisingly involved in the project, otherwise success would not be reached. It is not realistic to expect the industry to do it voluntarily. The producers should be encouraged by a well-prepared regulation that would gradually limit the amount of salt in products [22]. Although a stepby-step approach to a less salty taste in the initial reduction phase would have to work, in general, only a limited amount of salt could be reduced so that the product would not have an unpleasant taste. An atypical taste is a sufficient reason for not purchasing a product. Only when consumers are informed in terms of salt-reduced product, they can actually indicate a preference for a product that has a significantly lower salt level. Results of many studies show that salt perception is very important for consumer acceptability and a reduction in levels is hard to achieve without using salt replacers [53, 54].

A useful strategy to improve the palatability of reduced salt foods relies on the use of common salt replacing ingredients (salt substitutes). Among several options, potassium chloride (KCl) has proved to be an optimal nutritional ingredient for this purpose [55]. It provides similar properties as common salt (NaCl).

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Calcium and magnesium salts have many side effects; calcium chloride (CaCl₂) is salty but with many off-tastes bitter, tastes of MgSO₄ are usually perceived only at high levels; CaCl₂ can cause irritations on the tongue. Bidlas and Lambert's study results confirmed that in any foods, including cheese, bread, and meat, compared to NaCl, KCl calculated on a molar basis has an equivalent antimicrobial effect [56]. KCl has several unwanted side effects, the most important of which are relatively unnatural taints: bitterness, acridity and metallic taste [55, 56]. Commercially available substitutes are usually mixtures of salts containing sodium chloride, potassium chloride and magnesium sulphate. Not many studies [57, 58] have showed that partial substitution of NaCl by salt mixtures resulted in no negative effects on technological and sensory properties. Study on ground beef patties with the potassium chloride, magnesium sulphate and l-lysine hydrochloride salt mixture [57] did not find significant differences in taste compared to those with sodium chloride. However, the results of Gou et al. [59] are opposite. They evaluated the effect of substitution of sodium chloride with potassium chloride, potassium lactate and glycine on texture, flavour and colour of fermented sausages and dry-cured pork loins. Results confirmed that even partial substitution of sodium chloride with potassium chloride has generally negative effect on sensory properties and texture of a product.

Grummer et al. [60] have analysed the use of mineral salt replacers to reduce the sodium content in cheese; mixtures of NaCl or sea salt with KCl, modified KCl, MgCl₂, or CaCl₂ were used. Both calcium and magnesium chloride resulted in considerable off-flavours (bitter, metallic, unclean and soapy flavours), while potassium chloride did not result in any side effects.

We can conclude that side effects of alternative recipes are in correlation with nature of the basic material and concentration of salt substitutes. Consumed in excess, potassium may be harmful for some people. Many persons with kidney problems are unable to excrete excessive potassium, which could result in a risky situation what we already pointed in introduction. Persons taking cardiac, kidney or liver medications better check with their personal doctor before using salt substitutes instead of sodium.

Flavour enhancers are another category of ingredients used to replace the flavouring properties of salt. The most frequently used flavour enhancers are yeast extracts, yeast and vegetable protein hydrolysates, glutamic acid, monosodium glutamate and various nucleotides. Sausages and similar processed meat products are items in which lower-sodium content options have been successful. When flavour enhancers are used, structural functions of salt-soluble proteins need to be partially replaced by the addition of gums, soy or milk proteins and starches [61, 62]. Yeast extracts can be successfully added to any type of food. Functionally, they are used to cover any unwanted bitterness that addition of potassium chloride may have [62]. Hydrolysed vegetable and yeast proteins are flavour enhancers containing high levels of glutamate that also help initiate the umami taste. Partial replacement of salt with monosodium glutamate (<1.0%) did not result in negative sensorial properties of pork patties, although some studies [63] found high deterioration in quality, such as high cooking loss. Some of L-arginyl dipeptides were recently identified as salt flavour enhancers, in consequence, a possibility to reduce dietary salt intake without compromising palatability is raising [63].

Using spice blends and herbs is a promising alternative to improve the quality of reduced salt food products. By giving a spicy flavour and different aroma, these blends can also suppress or diminish negative effects caused by the use of potassium chloride and other replacers. In general, the alternative is easy to apply in industry, restaurants or at food preparation at home.

4. Development of adequate dietary habits in early childhood

Children's eating habits are established in the preschool period. This process is affected by family eating habits as well as preschool nutrition in kindergartens where children usually spend most of the day and consume most of their daily meals. Both, genetic predisposition and learned experience from environment influence children's preferences to salt. The review study [64] states that although the liking of salty food starts as unlearned response in early infancy, this liking soon develops as a result of repeated exposure to salty food. Generally speaking, a low exposure to salty food in infancy is associated with low preference for salty food [64]. No study suggested that decreasing the exposure to salt during infancy is associated with an increased liking of desire for salty foods.

Concern for the quality of food and children eating habits in preschool is, therefore, extremely important for the development and formation of eating habits later in life [64, 65]. Children learn about food through the direct experience of eating and by observing the eating behaviours of others.

Many authors tried to determine whether children find a food product with reduced salt content different enough to assess it as worse than the product with normal salt content [65]. Whether a food is liked or disliked is an important determinant of food intake, especially among children. Salt contributes to the taste of foods and makes them more enjoyable. Salt level has generally a positive impact on the intake of the target foods [66, 67]. Research found that 4-month-old infants identified and selected salted and not plain water, which indicates their salt taste perception mechanism. Six-month-old infants who were fed salty starchy table food retained their tendency towards salty foods later in childhood [68]. Results of the research showed that children aged 4 or more prefer salty foods to unsalted ones. Various studies have shown that after consuming food with reduced salt content for a certain period of time (up to 12 weeks), the preferred level of salt in food is lowered to such a level that foods with high salt content become unpleasant for the subjects [69]. Results of recent research provide evidence that promoting responsive feeding practices can alter the development of eating behaviour, sleep patterns and early self-regulatory skills, as well as reduce the early obesity risk [70]. In a study conducted by Kovač [65], the response of kindergarten children to less salty bread and the role of teachers and teacher assistants in the introduction of novelties into children's nutrition were studied. The purpose of the study was to identify the possibility of unnoticed reduction in salt content of bread as a basic food in the diet of preschool children. The children were not previously told to pay attention to the saltiness of the product. They evaluated the product as a whole. Using emotional faces, the children explained what they thought of the bread they ate. Despite the limitations of the hedonic evaluation, the results gave essential answer—children like bread with reduced salt content. Results demonstrated that 30% reduction in salt was not registered, while a 50% reduction in the salt content, compared to the original recipe, although noted, was not disruptive. These findings partially correspond to the results of Girgis et al. [71] whose results showed that a 25% salt reduction could be made without being noticed. However, the results of the study indicate that children also accept breads with a 50% reduction in the salt content, compared to the original recipe, although the results of some previous studies suggest that children prefer salty foods to unsalted ones [65]. Children did not associate those breads as 'less salty'.

When children go outside their familiar environment, they are influenced by role models. Children look up to different role models in order to help shape their behaviour in school, their relationships, and also making decisions concerning the food. The effectiveness of a child's role model in food preferences depends on the

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relationship between the child and the role model. For many young children, the most important role models are their parents and caregivers, older people or celebrities. Children also look up to other relatives, teachers and peers. Peers in kindergarten play an important role in shaping children's eating habits [65]. The results of survey [65] and its qualitative answers indicate that educational personnel have a significant impact on children's preference for a specific product or specific taste.

We can conclude that the environment young children live in, in particular, the persons with whom they are in close contact, is also important when formulating eating habits and influencing children's acceptance of reduced salt taste.

5. Conclusions

High salt intake is the major cause of raised blood pressure and accordingly leads to cardiovascular diseases. The overall goal of the global salt reduction push is a 30% relative reduction in average population salt intake towards the WHOrecommended level that is less than 5 g per day for adults.

The availability and accessibility of low-salt products is a very important part of salt reduction measures. Current approaches of reformulation include decreasing of salt by stealth, using salt substitutes, or using flavour enhancers. The most preferred option, especially when preparing food, is the use of fresh or dried spices to flavour the dishes. Consumer awareness of the need to reduce salt intake consumption should be enhanced by effective and accurate labelling and marketing of food. Creation of an enabling environment for salt reduction and promotion of healthy food and healthy dietary habits are the most promising measures especially in early childhood; at home, in kindergartens and schools. Such an approach could represent a basis for creating healthy dietary habits, which will be of particular importance for their whole life. WHO has stated that reducing salt intake has been identified as one of the most cost-effective measures countries can take to improve population health outcomes. Salt reduction measures will generate an extra year of healthy life for a cost that falls below the average annual income or gross domestic product per person. An estimated 2.5 million deaths could be prevented each year if global salt consumption were reduced to the recommended level [20].

Conflict of interest

The authors declare that no conflict of interests exist.

Salt in the Earth

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Section 3 Salt in Technology

Chapter 4

Short Review of Salt Recovery from Reverse Osmosis Rejects

Boopathy Ramasamy

Abstract

The membrane treatment is a physical separation which also generates considerable amount of waste, called as reject/concentrate. The reject/concentrate is more than three times concentrated than the feed water in terms of feed water salts. Recovery of valuables from reverse osmosis (RO) reject for its reuse of inorganic salts would be most obvious solution to eliminate environmental damage. In this report what are the available methods for the recovery of valuables from waste saline stream by selective crystallization method, chemical precipitation and physico-thermal route discussed in details. Also, methods to treat organic contamination in the residual solution through advanced oxidation treatment methods.

Keywords: reverse osmosis, salt recovery, reactive precipitation, crystallization

1. Introduction

The demand of potable water led to significant improvements in the membrane separation process in water and waste-water treatment. Especially for developing countries, the demand of water supply is increasing and no less provision to mitigate the challenges. The state and central governments agencies are formulating strategy through environmental policies to mitigate the water scarcity. During last three decades significant expansion and upgradation of membrane filtration have been happening around the globe to lower it production costs. In market, there are many custom made membrane technologies that are available for both domestic and industrial applications. Reverse osmosis is one of the important technologies among which has energy and cost effective membrane system for producing potable water from brackish and saline water sources [1–7]. RO process can generates 50–80% of water drinkable or dischargeable quality as permeate [7] and the balance 20-30% formed as RO reject or retentate or concentrate. Generally, concentrate is allowed to avoid membrane fouling, coagulation and flocculation process over membrane surfaces as it cannot be further purified due to high osmotic pressure. The common application of membrane separation processes comprising ultrafiltration and reverse osmosis for the disposal of reverse osmosis (RO) rejects through thermal evaporator or multiple effect evaporator.

1.1 Characteristics of membrane concentrate

Membrane separation is a physical process which involving the separation of particulate, and dissolved organic/inorganic compounds from a feed liquid using a semi-permeable membrane system. The feed stream is fractionated into two streams:

Parameters	Untreated waste water	Biological treated wastewater /RO feed	RO Permeate	RO Reject
pH* Total Dissolved	4.12-4.68	7.03-8.21	6.87-7.25	6.85-7.55
Solids Biological	7.67 ± 4.08	5.58 ± 1.80	0.25 ± 0.13	20.0 ± 6.14
Oxygen Demand ₅	2.09 ± 1185	0.10 ± 0.091	-	0.40 ± 0.32
Chemical Oxygen				
Demand	4.76 ± 2.42	0.43 ± 0.29	0.005 ± 0.007	1.53 ± 0.85
Sodium	1.60 ± 1.44	1.65 ± 0.53	0.05 ± 0.02	3.96 ± 1.67
Chloride	1.30 ± 0.42	1.30 ± 0.40	0.07 ± 0.02	4.99 ± 2.20
Sulphate	2.67 ± 1.58	2.31 ± 1.25	0.01 ± 0.02	5.55 ± 1.95
* All the values are	expressed in g/I	., except pH.		

Table 1.

Characteristics of untreated, treated, RO permeate and RO reject stream generated in leather industry.

(i) a permeate stream that contains the solvent (water) that passes through the membrane, and (ii) the reject stream known as concentrate, reject or brine contains the solute. The characteristics of this reject stream depend primarily on the membrane technology used, the quality of feed water, the percent recovery of water, the physico-chemical treatment methods followed for cleaning procedures. The volume of reject stream varies widely from 10 to 60% of the feed water volume [7]. However, the reject stream arises from industrial effluents such as textile, pharmaceutical and tanneries are turbid and opaque, may be due to the presence of micro and macro organic molecules and inorganic ions, such as chlorides, sulfates, phosphate, carbonate, bicarbonate, sodium, calcium, magnesium and other heavy metal ions [8]. The characteristics of RO stream generated in leather industry are presented in Table 1. The TDS of water is increased from 5.58 \pm 1.8 to 20 \pm 6.14 g/L in RO reject stream leaving product water with a TDS of 0.25 ± 0.13 g/L during separation process. The TDS concentration of RO rejects four fold higher than the initial TDS concentration. Similarly, concentration of sodium, chloride and sulfates ions were found to be increased significantly after RO separation process in reject stream.

1.2 Impacts of membrane concentrate discharge without treatment

Discharge of RO reject stream into sea/ocean is considered to cause the "sea desert" in vicinity to pipe outlet because of dissolved substance with high specific weight and thus sink in bottom of the sea/ocean, which severely affecting local marine biota. Marine species have been affected by the salinity of the brine discharged into the sea include grass prairies called such as *Cymodocea nodosa* and *Caulerpa prolifera* or red algae [9]. Direct land disposal of RO reject stream from effluent treatment plants caused soil and groundwater contamination by the diffusion of inorganic impurities from it, and thus soil and ground water are turned unsuitable for human consumption for their harmful or toxic substances. Hence, there has been constant exploration to manage the RO reject stream.

1.3 Options for membrane concentrate disposal

Various options have been reported for the disposal of RO reject stream generated in membrane separation. This option is discharge to surface water, deep wells,

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solar evaporation ponds, and thermal evaporators. The selection of technologies for the disposal of RO rejects is based on the prevailing environmental regulations, investment and maintenance costs, and site-specific conditions [10, 11].

The reduction of concentrate volume is being achieved by incorporating zero liquid discharge technologies. The concentrate streams after conventional RO are being evaporated in thermal evaporators to sufficiently dry inorganic salt. The most common way is vertical falling film brine concentrator followed forced-circulation crystallizer, where it is heated above its normal boiling temperature with steam through heat exchanger. It requires 65–80 kWh of power per 1000 l of crystallizer feed water. Crystallizers and spray dryers have been implemented at the commercial level to reduce RO reject stream into a solid product for landfill disposal. One or more evaporation steps could also be considered to recover small amounts of water from the most soluble salts in RO reject stream. The primary practical obstacle in implementing thermal evaporators is size and complexity of the equipment. In addition, evaporators and crystallizers are relatively complex to operate and high energy intensive process compared with other zero liquid discharge (ZLD) methods.

The evaporators and crystallizers are used to reduce the reject volume up to 5% of the feed volume and the rest 95% was reclaimed as distillate (water) after condensation. Generally, the reject stream generated from leather industry is evaporated in solar evaporation pans to reduce its volume (for small volume of discharge and making use of solar energy to reduce the cost of evaporation) or in a multiple effect evaporator (MEE) (for large volume of discharge) leaving behind a solid residue known as residue after evaporation (RAE).

1.4 Limitations on disposal of residue after evaporation generated from leather industry

The disposal of RAE onto secured landfill sites is banned by the pollution control agencies because the constituent ions are suspected to be leached into aqueous solution, and the treatability of leachate would be more difficult for its high salinity. Hence, RAE is collected and being stored in the storage yard without further reusable options in many textile and leather industries. The high concentration of mixture of inorganic and organic salts present in RAE restrains it from disposal [13, 14].

2. Desalting process for RO concentrate

Recovery of salts from RO concentrate is increasing for its environmental safe way to reuse of waste volume of reject. The change of solution temperature either by evaporation and cooling used to extract salts from concentrate has been widely used worldwide. In which, electro-dialysis, ion-exchange, eutectic freezing, and chemical processing are being practiced to recover salts from concentrate. Further, in advance hybrid systems which consisting of combination of two or more separation process techniques, such as the nanofiltration—reverse osmosis—thermal processes, are being deployed actively to increase the amount of extracted salt and reduce the final volume of reject.

Buckley et al. has proposed detailed routs for the management of RO reject [12]:

i. Use of engineering knowledge: incorporation of engineering unit operation/ process to reduce dissolved solids in the reject stream.

- ii. Chemical conversion of reject to products: chemical conversion of rejects to other reusable salts from waste RO reject.
- iii. Direct and indirect discharge of concentrated brine by dilution without affecting receiving environment.
- iv. Stabilization of concentrate to inert material: stabilizing the waste concentrate into chemically stable material.

2.1 Evaporation and cooling

Recovery of valuable salts or minerals can be obtained from RO concentrate or brackish water by altering solution temperature either by evaporation or cooling effect. There are reports on evaporators are being practiced in brine management, among which multiple effect evaporator (MEE) are most promising and cost effective. The MEE operate based on the principle of reducing the vapor pressure of solution within the system to permit boiling occurs at low temperature. The multiple effect evaporator feed water is boiled and pumped into tube side in the evaporator in series. The outcome of steam has been condensed over the tube wall of the evaporator and collected as water to reuse. The excess heat is further used for the boiling of inlet water.

In other way, vapor compression distillation (VCD) is used for the desalination process. In VCD inlet water is boiled through heater to vaporize and discharged through evaporative compressor. The generated vapor has been compressed and used as steam supply for boiling concentrate and the condensate product is obtained after compression process.

2.2 Electro-dialysis (ED) and ion exchange

Electro-dialysis system consists of anion-exchange and cation-exchange membranes are being arranged alternately in a large cell of compartment between an anode and a cathode. The influence of applied electric field, the various ions could migrate towards the electrodes based on its ionic charge. The membranes are permeable only to cations or anions, through which the water between the membranes are alternately depleted and enriched with salt ions. The cation membranes allow only positively charged ions to diffuse through them. Similarly, anion exchange membrane allows only negatively charge ions. Electro-dialysis is being considered used as a pre-treatment or a pre-concentration method for brine management [15–17]. This method of application significantly reduces the concentration of calcium or sulfate ions from gypsum crystallization during further evaporation [15]. However, fouling by colloidal material, organics, and bio-growth should be taken care for the effective and sustainable use of the equipment.

The performance of ion exchange processes based on packed bed column resin, which are generally organic resins that contains hydrogen ions and is capable of exchanging positive ions present in the feed water. The ion exchange processes are being studied, investigated, and applied for many desalting process over several decades [18–25]. However, this method of treatment applies only to low concentrations of salts containing brine water and its cost of regeneration is also higher.

2.3 Eutectic freezing crystallization (EFC)

In this process, the feed concentrate stream is frozen continuously until it reaches a eutectic temperature. The ice being forming.

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If the unsaturated concentrate is reaching its freezing point. At the specific eutectic point of crystallization, the brine salt is crystallized out as product. The energy required for the EFC process are found to be very less than the conventional method of evaporative and cooling crystallization process and its theoretically possible way to complete the conversion of concentrate water into water and solidified solutes.

Through this route magnesium sulfate heptahydrate (MgSO₄·7H₂O) from a magnesium sulfate industrial stream is being recovered using EFC process [26, 27]. In which MgSO₄·12H₂O was formed in the crystallizer and after recrystallization MgSO₄·7H₂O is formed spontaneously. In addition to EFC, coupling of cooled disk column crystallizer (CDCC) helps to recover CuSO₄ crystals from copper sulfate solution [28, 29]. The cost towards energy required for EFC can be reduced up to 70% than conventional evaporative crystallization processes, further 100% conversion of concentrate into water and salt separation is achieved by this route.

2.4 Chemical process

Recovery of CaCO₃ from nanofiltration reject is being achieved by reactive precipitation on addition of NaHCO₃/Na₂CO₃ aqueous solution [30]. Similarly, recovery of MgSO₄·7H₂O from the reject from seawater nanofiltration, Ca^{2+} ions were precipitated as carbonates by reaction with NaHCO₃/Na₂CO₃ to get calcium sulfate by precipitation, Sodium-bi-carbonate solutions are being produced by reactive transfer of carbon dioxide into sodium hydroxide solutions. This technique has been used successfully to recover magnesium sulfate from sulfate rich brine, rock forming minerals, and salty lake water [31–33]. There are many sequential extraction of salts from rejected brine thus which high concentration of dissolved sulfate, potassium, and magnesium salts are being separated through multiple effect evaporator and cooling crystallization method, reactive precipitation methods [15, 28]. The use of lime favors selective separation of magnesium hydroxide from concentrate solution and thermal calcination of concentrate having sodium sulfate helps to recover Na₂SO₄ from wastewater [34]. The reject generated from textile dyeing industry contains large amount of Na₂SO₄ and thus being recovered through multiple effect evaporation and/or calcinating the concentrated reject in a muffle furnace at a temperature range of 300 and 800°C [35].

2.5 Extraction of potentially profitable material from RO rejects

2.5.1 Calcium

The recovery of calcium from RO reject is done to avoid secondary RO scaling [36–38]. Bond and Veerapaneni [36] have developed detailed methodology for the recovery of calcium carbonate by chemical precipitation, in particular to separate calcium during desalination. Several other researchers have evaluated fluidized bed crystallizers for the production of calcium carbonate pellets from RO reject [36, 39], further studies have been reported on influence of anti-scalants, impurities, metals, and ions on calcium carbonate precipitation [40–42]. The concentration of calcium ions in seawater and desalination reject is relatively high, through this calcium carbonate pellets has been prepared from brackish water in Southern California [39]. However, the extraction of calcium sulfate from RO reject has not received significant attention, due to low price of commercial grade gypsum. Also, the mechanisms of calcium sulfate precipitation have been observed to form scaling minimized equipment failure in separation process [43–46]. The ion-exchange resin is being used to selectively extract calcium sulfate salts from RO reject by control-ling the pH of the mixture of anion and cation regeneration solution.

2.5.2 Magnesium

The main unit processes used for the extraction of magnesium is evaporation cum crystallization, precipitation, and ion-exchange. Ohya et al. [47–49] proposed a series of integrated processes (crystallization, electro-dialysis, ion-exchange) to recover salts of calcium carbonate, sodium chloride and magnesium sulfate from RO reject. Drioli et al. identified a process of membrane crystallization/distillation to separate out various inorganic salts from reject streams from an integrated NF/ RO process [30, 50]. In Russia, a large scale extraction plant is also being operated for the recovery of magnesium from seawater using ion-exchange, and extraction of magnesium from RO reject from seawater desalination system.

2.5.3 Potassium

Worldwide potash consumption is increasing every year approximately at a rate of 3% due to population growth and other increased demand for fertilizers [51]. The main source of potash production is done by conventional shaft mining or deep-well solution mining process techniques. Currently, potassium is being produced from seawater as a byproduct from solar salt evaporation. As an alternative to solar evaporation/precipitation, several researchers have suggested that, potassium could be produced from RO reject using an evaporation/crystallization process [52, 53]. The extraction of potassium is done using natural zeolite (clinoptilolites) ionexchange materials which has high exchange capacity for potassium through a twostep dual-temperature process.

2.5.4 Sodium

The production of sodium compounds from desalination reject is obtained through evaporation technologies, followed by crystallization [54, 55], membrane crystallization [56, 57], electrodialysis followed by multiple effect distillation (ED/ MED) [54–58], and evaporation ponds [59, 60]. Membrane crystallization (MCr) is being practiced to produce relatively pure salt crystals from a synthetic NF reject solution having calcium and magnesium [66]. Tanaka et al. [17] developed an electro dialysis process for the production of salt from seawater reverse osmosis (SWRO) reject with less than 80% energy than conventional process. A similar process developed by Davis [47] on electrodialysis metathesis which has integrated evaporator unit to separate out sodium sulfate and sodium chloride [61]. The SAL-PROC process (Geo-Processors USA Inc) is being used to produce sodium chloride, calcium sulfate, calcium chloride, and magnesium hydroxide from concentrated solutions including brackish water reverse osmosis (BWRO) and seawater reverse osmosis (SWRO) concentrate.

2.5.5 Nitrogen

In general, RO reject stream was found to be more than 40 mg of nitrogen per liter. The available method to recover ammonia-nitrogen by struvite precipitation, since extraction of ammonia is economically poor.

2.5.6 Sodium chloride

The SWRO reject through either electro-dialysis (ED) or electro-dialysis reversal (EDR) step is sufficient to separate out impurities and that the salt produced is fit for human consumption; however, there is little information available on final

product purity using this approach Tanaka et al. [17]. Electrolytic method of simultaneous separation of chlorine and sodium chloride has good market potential for the effective management of RO reject. Melian-Martel et al. [62] used membrane electrolytic cells to recover chlorine, hydrogen and sodium hydroxide from seawater RO reject. Boopathy et al. reported separation of sodium chloride from the RO reject generated in leather processing industries through reactive precipitation techniques [63].

2.5.6.1 Precipitation of sodium chloride from evaporated residue of RO rejects

The movement of ions during precipitation is expressed in the form of chemical equations as given below:

$$RAE + H_2O \rightarrow Na^+, Cl^-, Ca^{2+}, SO_4{}^{2-}, Mg^{2+}, Org^-/Org^+, H_2O$$
(1)

$$\begin{aligned} &(\mathrm{Na}^+, \mathrm{Cl}^-, \mathrm{Ca}^{2+}, \mathrm{SO_4}^{2-}, \mathrm{Mg}^{2+}, \mathrm{Org}^-/\mathrm{Org}^+, \mathrm{H_2O}) + \mathrm{HCl}_{(g)} \\ &\to \mathrm{NaCl}_{(S)} + [\mathrm{H_3O}]^+ + \mathrm{Na}^+ + \mathrm{Cl}^- + \mathrm{Ca}^{2+}, \mathrm{SO_4}^{2-}, \mathrm{Mg}^{2+}, \mathrm{Org}^-/\mathrm{Org}^+ \end{aligned}$$

The residue of RO rejects has been dissolved in water to prepare saturated RAE solution as shown in Eq. (1). The increase in ionic concentration in the saturated solution shifts the reaction to backward direction by common ion effect. In this study, hydrogen chloride gas was prepared and purged to increase the concentration of Cl^- ions in the RAE solution. The incremental increase in Cl^- ion concentration shifted dynamic equilibrium by increasing the ionic product of Na⁺ and Cl⁻. The ionic product of Na⁺ and Cl⁻ exceeded the solubility product of sodium chloride [solubility product of NaCl, (K_{sp}) is 36 (mol/L)²] and thus the precipitation of sodium chloride was achieved from the saturated solution of RAE as illustrated in Eq. (2). The schematic flow diagram of separation of sodium chloride from RAE solution generated in leather industry has been illustrated in Figure 1. First saturated RAE solution has been prepared by dissolving 60% (w/v) RAE in water and the insoluble grits are removed after gravitational settlement. The clear supernatant solution was taken in reactive precipitation reactor and HCl gas has been purged continuously for the reactive precipitation of sodium chloride. The required HCl is being prepared and used spontaneously. Since the prepared HCl gas cannot be stored, if we store which may condensate and turn into liquid form. After successful purging of HCl gas the sodium chloride salt is separated out from the solution by reactive precipitation as per the reaction given in Eq. (2).

2.5.6.2 Effect of HCl gas injection time and RAE concentration on NaCl recovery

The HCl gas purging time for the separation of sodium chloride from RAE solution was carried out by varying time from 0.5 to 3 min at its native pH, 8.0 and temperature, 40°C. The optimum condition for the recovery of NaCl is achieved within 3 min of contact time as shown in **Figure 2a**. The optimum time of 3 min of contact time yield 81% recovery of sodium chloride. This is explained that the equilibrium was established i.e. the rate of precipitation of NaCl becomes equal to the rate of dissolution of NaCl in the solution. The mass of precipitated NaCl at the optimum time was 26.7 g with 81% recovery with respect to the dissolved salt concentration (solubility of NaCl is 35 g in 100 mL of water).

The concentration of RAE [40-65% (w/v)] was varied to identify the effect on precipitation of NaCl. The results in **Figure 2b**, shows that the percentage of salt recovery increased with the increase in concentration of RAE. In general, precipitation depends on the concentration of dissolved ions in solution. As the initial

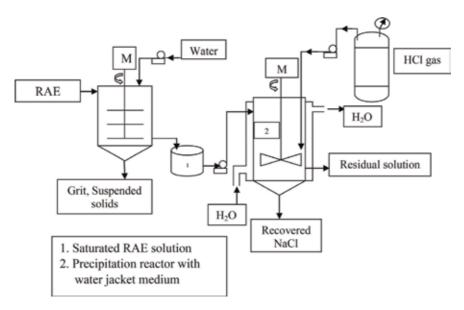


Figure 1.

Schematic flow diagram for the selective precipitation of sodium chloride from RAE generated in leather industry.

concentration of RAE increased, the dissolved ions concentration was also increased in the solution and reached the saturation limit at concentration 60% (w/v). The maximum amount of NaCl precipitation was achieved with 82% recovery for 60% (w/v) RAE solution. Further to evidence that the recovered salt is NaCl, SEM and EDAX analyses were carried for the recovered NaCl as shown in **Figure 3**. The surface morphology of RO reject looks aggregated mass like structure and thus may be due to mixture of many inorganic and organic salts. This is confirmed by EDAX spectrum shows presence of inorganic salts. However the recovered salt has a cubical structure, which is a characteristic morphology of sodium chloride and thus it claim that the recovered salt is sodium chloride. Further EDAX spectrum peak observed only for Na and Cl and thus confirmed that the recovered salt is NaCl.

2.5.6.3 Mass balance on preparation of saturated RAE solution

mass of RAE + deionised water
$$\rightarrow$$
 saturated RAE solution + grit
0.6 kg + 1 kg \rightarrow 1.32 kg + 0.28 kg (3)

The mass of saturated solution of RAE was 1.32 kg, obtained by dissolving 0.6 kg of RAE in 1 l of deionized water. The undissolved grit (0.28 kg) mainly consists of sand, lime and clay being non-hazardous in nature, which can be disposed off onto secure landfill.

2.5.6.4 Mass balance on precipitation of sodium chloride

saturated RAE solution + HCl gas
$$\rightarrow$$
 precipitated sodium chloride
+ residual solution1.32 kg + 0.105 kg \rightarrow 0.268 kg + 1.157 kg
(4)

The maximum precipitation of sodium chloride of 0.268 kg was resulted from 11 of saturated RAE solution under the optimized conditions.

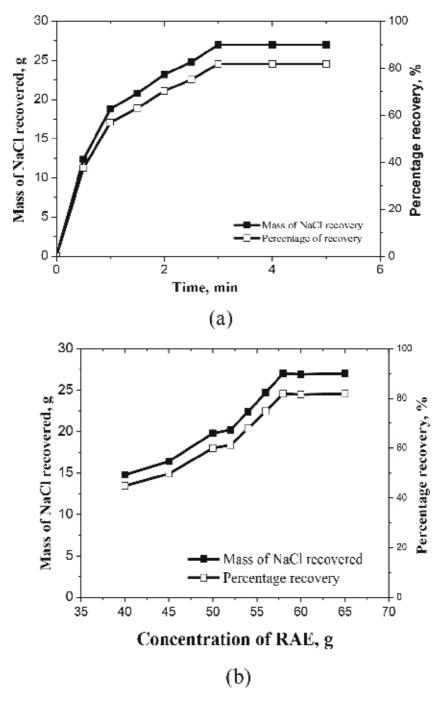


Figure 2.

Precipitation of sodium chloride (a) effect of time (conditions: pH, 8.0; temperature, 40° C; mass of RAE, 60% (w/v)), (b) effect of concentration of RAE (conditions: time, 3 min; pH, 8.0; temperature, 40° C).

The proposed process for the management of RAE was relatively lower in cost than the other disposal methods, and also the process has the scope to recover sodium chloride. The proposed process recovered 0.203 kg of NaCl from 1 kg of RAE. The resulted acidified supernatant solution (RAS) was considered for separation of sulfate ions as calcium sulfate. The sulfate ion in the RAS solution and synthetic RAS solutions were separated by the addition of various neutralizing

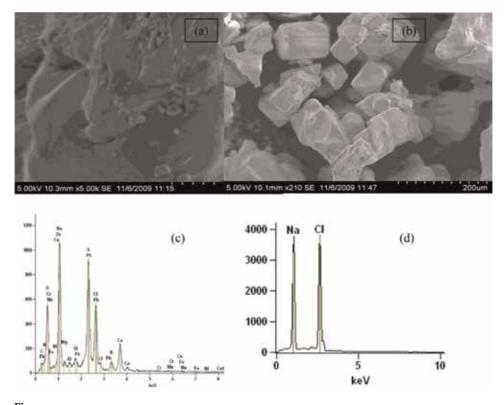


Figure 3. Scanning electron microscopy images of: (a) RAE, (b) recovered NaCl from RAE and energy dispersive X-ray spectra of (c) RAE, (d) recovered NaCl from RAE.

agents. Among the selected neutralizing agents, $Ca(OH)_2$ was effective for the separation of sulfate ions from the RAS solution and synthetic RAS solutions. The total cost for the management of 1 kg of RAE by the proposed process was 0.155 USD while the cost on landfill disposal was 0.11 USD. The recovered salts proposed to be reused for the hide/skin presentation in slaughter house [63].

2.6 Integrated process

Salt recovery or recovery of valuables from concentrate are being effectively done through an integrated approach by combining one or more separation process which serve as a pretreatment or post treatment step [64]. In electro-dialysis for concentrating reject brine solution, multi-stage flash being employed for desalting water, and crystallization for recovering salts, or with RO may be used instead of the multistage flash evaporator [65]. In another approach, RO reject are being supplied to an ion-exchange membrane electrodialyzer as post treatment, and then concentrated brine from the electrodialyzer is sent to a multi-effect vacuum evaporator to crystallize the salts present in water stream [58]. Variety of inorganic salts is also sequential extracted from rejected brine for the high concentration levels of dissolved sulfate, potassium, and magnesium salts through multiple effect evaporation and cooling of saline wastewater, chemical reactions, crystallization, washing, and dewatering. The processes developed by researchers to recover various valuables from RO reject are presented in **Table 2**. The combined process helps to recover both salts and water from textile rejects [66–68].

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Sr.No	Processes	Recovery of	
		valuables	
1	EDR, precipitation, evaporation	Br2, Mg(OH)2, NaCl	Davis, 2006
2	ED/EDR, MSF, crystallization	NaCl	Turek, 2003
3	ED/EDR, MED, crystallization	NaCl	Tanaka et. al.,
			2003
4	ED/EDR, MSF, MVC	NaCl, Mg, Cl ₂ ,	Kim, 2011
	precipitation, NF, Mcr	NaOH, CaCO ₃	
5	SAL-PROC process,	CaSO ₄ , Mg(OH) ₂ ,	Ahmed et.al.,
	precipitation, evaporation	NaCl, CaCl ₂ ,	2003
		Na ₂ SO ₄ , CaCO ₃	

Table 2.

Recovery of valuables from RO reject through integrated approach.

3. Conclusions

The thermal routes of evaporation are the most studied process techniques for the recovery of inorganic salt from RO reject; however, membrane separation techniques are cheaper for the recovery of product quality. The membrane separation process has generates reject volume which need further treatment. The ion-exchange, electro dialysis, eutectic freezing, and chemical reaction are also being explored more in recent times for its cost and efficiency on recovery of valuables from the reject stream. The integrated systems are being studied by combining one or more unit operation or process techniques to increase the recovery percentage of valuables. The selection of process or techniques may be selected based on the salt to be recovered, geological, hydrological, climatic, and economic conditions for its local specific.

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Conflict of interest

There is no conflict of interest with any funding agencies.

Nomenclature

RO	reverse osmosis
kWh	kilowatt hour
ZLD	zero liquid discharge
MEE	multiple effect evaporator
RAE	residue after evaporation
VC	vapor compression
ED	electro-dialysis
EFC	eutectic freezing crystallization
CDCC	coupling of cooled disk column crystallizer
NF	nano filtration
MED	multiple effect distillation

MCr	membrane crystallization
EDM	electrodialysis metathesis
BWRO	brackish water reverse osmosis
SWRO	seawater reverse osmosis
EDR	electro-dialysis reversal
RAS	resulted acidified solution
USD	US dollar

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Chapter 5

Upward Capillary Mass Transfer as a Process for Growing Concentration Zones

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Abstract

The natural process of circulation of ground and atmospheric water through evaporation from the surface and precipitation from the atmosphere to the surface leads to colonization of the surface soil layer. The main source of salts in the soil is groundwater. Groundwater reaches the surface soil layer and evaporates, and its constituent salts accumulate in the soil. The concentration of salts on the surface can reach to 100% (crust). This process is widespread. Vast areas of solonetzes are located in deserts and semideserts of Asia, Australia, South America, northern Africa, and the western United States. This natural process can be applied in the field of extraction of natural resources from the bowels. The process of salting the soil surface is low and gradual and is subject to study for possible use in technological solutions for the extraction of minerals. In this chapter, the authors intend to show the beneficial advantages of the phenomenon of surface salinization of the soil layer. Water-soluble salts due to their high mobility allow directional mass transfer along the capillary system of the soil and deposition in the aeration zone. However, the utility does not belong to plant biota. This phenomenon can be effective and safely used in the creation of near-surface concentration zones. The natural process of the filtration upward of salt solutions from the depths of the massif to the surface will purposefully carry out the transfer of valuable components with deposition in the area of the evaporation barrier. The speed of the process of ascending capillary mass transfer is technologically low but rather suitable as a preparatory operation at the place of storage of industrial wastes and burials and in the formation of zones of high concentration of small substandard natural mineral deposits. The chapter presents the results of experimental studies of ascending mass transfer of useful components from the waste material of the concentrating production of nonferrous metals.

Keywords: upward mass transfer, geochemical barrier, soil capillaries, aeration zone, upward fluid, sedimentation, vapor barrier, leaching

1. Introduction

Many natural minerals that form mineral deposits during oxidation become water-soluble like the conversion of metal sulfides to oxides. Mineral deposits

located near the surface are exposed to oxygen from the atmosphere, and minerals oxidized (hypergenesis) become water-soluble and can be subjected to water leaching by filtration mass transfer. Hypergenesis is a strong geological process of chemical and physical transformation of minerals and rocks in the upper parts of the Earth's crust and on its surface under the influence of the atmosphere, hydrosphere, and living organisms at temperatures characteristic of the Earth's surface. Among them, hypergene transformation refers to the number of common and most productive geological processes. Hypergene transformations are very dynamic in the geological sense, but very slow in the technological sense. The process of geological formation of such deposits consists in the mass transfer and deposition of useful components on physical and geochemical barriers. The study of these processes and their application may be appropriate as a preparatory process before the extraction of minerals by common technological technologies. The directed application of geological processes in the technological foundations of the structural and material transformation of the array will lead to the achievement of standards to the existing capabilities of technology.

The water-based mass transfer occurs by dissolving salts with water from the capillary surface, moving as a salt solution and precipitating salt from the solution under the influence of physicochemical factors. Water-soluble forms of mineral compounds (salts) are involved in such mass transfer. The shape, content of non-ferrous oxides, the location, and size of ore concentration zones depend on the conditions of the source and the potential of the subsoil (water content of the subsurface massif, pressure gradient, mass structure porosity, etc.), which causes the fluid to move. Natural geological ore concentration zones do not always correspond to the technological conditions of mining. Sometimes it is required to look for the presence of driving factors or, if it is possible, to create them.

The principle of filtration formation of concentrated zones is a kinetically dynamic geological process [1]. It involves three operations: transfer of watersoluble mineral compounds to the fluid, movement of the fluid in the capillary medium of the massif, and deposition on the physical or geochemical barrier. Due to the high kinetics (in geological sense) of this process, it can be applied in the field of mining as a preparatory stage—bringing the parameters of the subsoil section to effective technological conditions. The process due to the inconsistency of the speed by the technological processes should be brought to a separate—preparatory stage. The whole complex of leaching operations must be assessed in studies of the potential formation of artificial concentration zones.

The presence of water-soluble compounds, the minimum and maximum concentrations of the studied solutions, and the kinetics of the capillary motion of fluids are very important in the complex for the leaching process. If there are no such mineral compounds, they must be created.

The most suitable object for using such an approach is enrichment waste zones. The waste flotation enrichment of Norilsk mining was taken as the object of study in such objects in which there is always a useful component in a dispersed form. The whole object of tailing dump is located on the surface and is isolated from the natural environment by an engineering dam. The waste mass is flooded and finely dispersed; as a rule it has water-soluble metal oxides, and with the access of oxygen from the atmosphere, oxidation of sulfides is possible with the formation of watersoluble minerals. These conditions completely provide guaranteed controllability of mass transfer. In order to assess the feasibility of the filtration formation of oxidized ores of nonferrous metal concentration zones, expert studies were conducted on directional upward mass transfer for the conditions of the tailing dump of waste flotation enrichment of the Norilsk mining and smelting hub.

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According to the laws of communication of groundwater with the atmosphere, the solutions of groundwater can move upward through the evaporation zone to the surface by capillary action mechanism. Along with this, a very powerful natural mechanism for solution flow through a massif enables upward vertical movement due to the pressure gradient between the surface and the fluid level in the water table. The reason for the formation of a pressure gradient consists in evaporation of water from the surface of the array. The upward fluid flow rate is controlled by all the forces in the capillary system and the humidity [1–3]. Water evaporation from the solution increases the concentrations of the useful mineral compounds along the direction of flow in the surface aeration zone. When these concentrations exceed the solubility limits, the useful compounds are deposited in the column. Different mineral compounds have different concentration limits in the solution; therefore, the compounds can be selectively precipitated at different heights in the aeration zone. Essentially, the aeration zone acts as a natural evaporation barrier. Selective enrichment can be achieved due to the physical nature of the capillary action in the upward direction and the deposition surface. Partial laws for the upward capillary rise of solutions were formulated in studies of agricultural soils [4–9]. The soil particle size and stratification structure were shown to influence the capillary action considerably [9–14]. To leach valuable compounds in a column, their velocity and the large contact surface area between the solution and solid material in the capillary system are important [15]. These parameters must be optimized to ensure that the extraction is complete and the upward capillary leaching process can be controlled. Upward capillary leaching was studied by investigating the upward capillary flow of solutions with access to the column surface and of the solutions that deposit salts in the near-surface aeration zone. The concentration of precipitated salts was estimated by samples at different levels of the evaporation barrier in the columns.

The leaching process is one of the main technological solutions for recovering useful components from poor ore [16, 17]. Leaching can sometimes be the only and therefore the most important method for recovering components from poor-quality ores. Now, underground leaching and heap leaching are well-known technological solutions that are widely used for metal ores [18–21] and nonmetallic minerals [20] (such as Chilean saltpeter). Very often the leaching is one of the only effective extraction technologies for removing valuable components from ores given that their contents have been decreasing recently. In fact, the United States and Australia are world leaders in the gold mining industry through the use of leaching technologies. Heap leaching technology is the most widely used. In heap leaching, gravity-driven fluid flow through the column is exploited. For each type of ore, the leaching technological process must be optimized. For example, Padilla et al. [20] analyzed two parameters of heap leaching, the leaching time and heap height, to determine the best performance indicators. Ghorbani [23] examined the effects of the surface characteristics and mineralogy of particles in the heap leaching process. The mineralogical composition of the ore and the leaching reagent properties control the transfer kinetics of useful species between the solid and liquid phases, demonstrating the applicability and efficacy of leaching under specific conditions. In addition to the dissolution of the column material in the fluid and precipitation of valuable compounds in the column, the fluid flow kinetics and direction are also important parameters in p leaching technology. Depending on the initial concentration of solutions and the size of a subsurface aeration zone, the precipitation distribution can be varied, and these very parameters can play a key role in monitoring of component concentrations.

As for technogenic formations, the evaporation barriers can be helpful for purposeful concentration of components in tailing dumps to mitigate the environmental load. The presence of salts with different solubility in solutions at evaporation barriers makes it possible their selective extraction. The filtration type of natural deposits plays an important role as a mineral source of minerals. Geological processes of filtration mass transfer formed quite a few deposits with a rich content of useful components [24].

In geological filtration processes, the main solvent and main carrier is water and aqueous solutions of salts. The possibilities of water mass transfer of useful components for low concentrations in the field of mining and hydrometallurgy in the process of upward capillary movement were carried out in the conditions of an array of separate wastes from the enrichment of nonferrous and noble metal ores. Low content of nonferrous and noble metals in tailings can identify the diffuse distribution of components in the bowels of the Earth. In addition, the mining industry has created a huge amount of waste enrichment. All of them are located on the surface of the Earth and have an area many times larger than the area of the deposits themselves. The overwhelming part of the man-made mining waste has a high degree of danger. The total reserves of useful components in industrial waste are several times higher than the proven reserves in the bowels of the Earth. Carrying out extraction is currently unprofitable due to its low content. There is a great temptation to find and launch the natural process of structural and material transformation of the array, which forms the concentration zones of useful components from the diffuse state that will be profitable for the existing technological level. This approach will make a profit and eliminate toxic environmental pollution. With the application of this solution, experimental studies of the ascending capillary movement of aqueous solutions of the soil layer near the surface were carried out. Nature uses this process extensively and suggests a variety of technological solutions.

The mineralogical composition of the ore and the leaching reagent properties control the transfer kinetics of useful species between the solid and liquid phases, demonstrating the applicability and efficacy of leaching under specific conditions. In addition to the dissolution of mineral materials and its movement in the column and precipitation of valuable compounds in the column, the kinetics and mass transfer direction are also important parameters in p leaching technology. To assess the applicability of the natural mechanism, only water and aqueous solutions of salts were used in technological solutions. The upward velocity of the fluid flow depends on the pressure gradient, which is the driving force of in situ leaching.

2. Materials and methods

2.1 Capillary rise with fluid release of the column surface

Drinking mineralization water was used in mass exchange experimental studies. The results of studies have been obtained on the directional upward mass transfer of water-soluble salts of nonferrous and noble metals in the conditions of the tailing dump of mineral processing. The speed and variability over time of the directed capillary ascending rise of aqueous solutions were obtained for dispersed materials of enrichment waste. The kinetics of formation of water-soluble salts of nonferrous and noble metals was evaluated for the tailing dump. This process is basic of the water leaching for enrichment waste. The experiments were performed using the setup shown in **Figure 1**. The core polycarbonate column had a height of 1.5 m and a diameter of 110 mm. The bottom of the column was connected to a solution tank by

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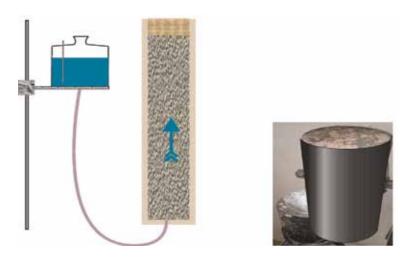


Figure 1. Installation of the upward movement of water-soluble solutions.

a flexible pipe. The solution tank, which was a Mariotte bottle, was mounted on a platform that could be moved along the entire column height. The material to be tested was charged in the column. The solution was fed to the column at a constant feed rate through a bottom opening. The feed rate was controlled by the solution level in the Mariotte bottle, which was set to the height of the material surface in the column. In the first pilot version of the continuous upward flow system, the column was loaded with flotation tailings from the Norilsk industrial hub. These flotation tailings consisted of finely crushed ore with a predominant fraction particle size of 0.05-1.2 mm. The main minerals in the ore were rock-forming minerals, i.e., aluminum silicates (muscovite, illite, serpentine) and quartz. The ore also contained pyrrhotite, chromite, and minor amounts of chalcopyrite, calcite, brucite, and pentlandite. The sulfide mineral content was as high as 10%. The flotation tailings looked like a gray sand. The nonferrous and platinum group metal contents of the tailings were 0, 34% Cu, 0.39% Ni, 0.019% Co, 1.3 g/t Pt, 3.1 g/m Pd, and 0.23 g/t Au (atomic absorption spectroscopy). The content of useful components in the materials of the experiment was obtained by chemical analysis of its own chemical laboratory and was compared with the values of the chemical laboratory of the Norilsk mining and smelting hub. The initial working solution had a mineral content similar to that of mineralized drinking water at $pH \sim 7.0$ and flowed through the capillaries in the material to the surface. The solution that reached the surface was removed for extraction. The useful component content of the flotation tailings in the column was monitored by serial geochemical analysis during the experiment by the method [14], which showed that the exchangeable fraction consisted of readily water-soluble compounds and accounted for the largest percent of the noble metal species (31–46%). Crystalline Fe and Mn oxides constituted the second largest fraction of the tailings (20–30%). The copper, nickel, and cobalt sulfide mineral contents were in the range of 13–27% and, together with the oxide phases, accounted for 43-61% of their total contents. The nonferrous metal content of the exchangeable fraction ranged from 4 to 10% (Figure 2). During the entire experiment, which was conducted for 15 months, the level of water was at the same level using a Mariotte vessel to evaluate fluid kinetics over time. The water solution at the surface was periodically analyzed for Cu, Ni, Co, Pt, Pd, and Au. In addition to these experiments, experiments in which an absorbent layer was placed on the surface were performed. This layer was designed to collect the product solution. A

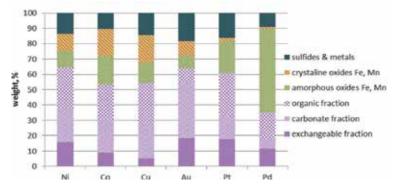


Figure 2. Geochemical phase analysis of the metal distribution in the feedstock.

series of experiments (**Figure 1**) in which the starting feed solution level was decreased relative to the material surface height in the column were performed with the hygroscopic layer.

2.2 Capillary selective precipitation in the vapor barrier

To assess the distribution of sediment in the aeration zone in the quartz sand massif, nickel and cobalt nitrates of different concentrations were used. Experimental studies in which the feed solution level was either variable (level varied from bottom to surface) or fixed based on the calculated capillary rise height were performed in a pilot plant (Figure 1). The experiments were carried out with the supply of aqueous solutions of cobalt and nickel nitrates of different initial concentrations. The Co and Ni nitrate concentrations of the feed solution were varied to assess the distribution of salts on a surface of the aeration zone. The column was filled with quartz sand with a narrow particle size range, and the capillary radius of the material, which was chemically neutral for the Ni and Co nitrate solution, was calculated. The experiment was conducted over a 15-month period. During the entire experiment, the solution filtration speed and nitrate concentration distribution along the column height were estimated. The concentration distribution in the column material was determined by periodic testing. The effect of the column surface (atmospheric pressure, temperature, and humidity) on the upward fluid flow rate was also evaluated, which correlates with [13].

3. Kinetic of filtration capillary moving

A series of experiments to study the kinetics of the ascending capillary rise of the solutions were studied on a laboratory bench. The zone of the capillary hoist of solution works as an aeration zone with variable humidity in height. The upward capillary mechanism of fluid and pressure gradient forces stimulates the solution hoist through pores to subsurface areas of the massif. When the solution passing through the aeration zone, the salt concentration grows due to water evaporation with follow-up. Precipitation solid phase in the porous mass medium [8]. The mass humidity varies from complete inside to atmospheric levels in the aeration zone. For this experiment the aqueous solutions nickel nitrate and cobalt have been used. Nitrates have different initial concentrations: from 0.34 Mol/l (unconcentrated) to 2.75 Mol/l, (close to extremely saturated concentration). Evaporation proceeded at different capillary hoist velocities. The rate of evaporation was controlled by the temperature of

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the array, the temperature of the atmosphere, and humidity, taking into account the atmospheric pressure. The correlation between speed and temperature (from 18 to 30°C) and atmospheric humidity is proportional, and the coefficient is 0.70–0.85 (linear with varying atmospheric pressure). Experiment imitates condition migration and evaporation in summer in moderate climate regions of Russia. In other test conditions, the capillary motion of the solutions was intensified by heating of massif material up to 50°C in the upper zone and by subsurface blowing with a directed warm air jet at 5–7 m/sec to imitate speedy evaporation in hot climate conditions. The massif structure and variations of mineral content of material in experimental columns were comprehensively analyzed in terms of structure to evaluate salt precipitate distribution in the porous aeration zone. The theory of the salt precipitation phenomenon with crystallization from the capillary mouth is developed in [12]. Condition for salting out can be approximately written as:

$$a \leq \frac{D}{L} ln\left(\frac{C_{sat}}{C_0}\right) \tag{1}$$

where a is evaporation rate, cm/s; D is coefficient of salt diffusion in a solution, cm^2/s ; L is capillary length, cm; C_{sat} is concentration of saturated solution, g/cm³; and C_0 is initial solution concentration, g/cm³.

Formula (1) determines the evaporation rate, which excess of concentration can cause crystallization in the capillary mouth. At the high evaporation rate, the solution concentration on the capillary surface due to size changes can exceed C_{sat} limit and result in the formation of precipitate and salt crystals. As for solutions and low evaporation rates, the solution concentration nearby retreating meniscus C_m should remain constant and equal by theory [15]:

$$\frac{c_m}{c_0} = 1 + \left(\frac{\pi\beta}{D}\right)^{1/2} \tag{2}$$

where β is an evaporation factor, cm²/s. The direct experimental verification confirmed the correctness in terms of the theory [11].

In the course of long-term experiments on rising capillary filtration, the kinetic regularities of lifting solutions in the aeration zone were obtained (**Figure 2**). In the initial period of long-term experiments of ascending filtration of solutions, periods with a high rate of rise were recorded. The real velocity of the solution in the array repeatedly (up to 7 times) exceeded the calculated value (Darcy's law) [21, 22]. It is difficult to unambiguously explain this effect; most likely this may be due to the unsteady capillary flow of solutions due to a change in viscosity when external factors are superimposed.

The experiment showed us that at low evaporation rates (t $\leq 22^{\circ}$), the salt crystallization at surface was visually observed since 43 days from the start of the experiment. **Figure 3a** shows a dependence obtained for a solution motion rate at capillary hoist of concentrated nickel nitrate solution at the initial stage of the test. It is obvious that when the solution concentration does not exceed the saturated solution concentration and no crystallization is observed, the evaporation rate varies rather intensively, and evaporation mode can be estimated as unstable. Since the crystallization starts, the evaporation rate reduces in regular linear fashion. It is a long-lasting process at rather slow crystal growth, perhaps, due to the fact that a precipitate narrows capillary section, reduces actual evaporation surface, and diminishes the evaporation rate. Under the theory (2) the salt concentration nearby meniscus should be constant with probable partial dissolving of fresh-formed crystals. This, in its turn, increases evaporation rate and growth of concentration.

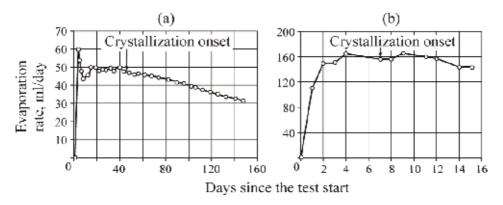


Figure 3.

The evaporation rate for aqueous Ni(NO₃)₂ solutions from porous material under different evaporation conditions: (a) $t = 22^\circ$; (b) $t = 52^\circ$, blowing velocity 5–7 m/s.

Crystals increase in volume and the evaporation surface reduces again. This mode of variability in crystal volume lasts for a long term. For 2 years of the experimental work, the solution motion rate stabilizes at 0.4–0.7 mm/h level with possible linear reduction within 3–5% per year. The test results confirmed theoretical conclusions made in [14], viz., in the course of evaporation, the growth of solution concentration is compensated with diffusive diversion of electrolyte in the depth of a capillary, where the evaporation rate tends to lower on the regular basis. The reduction in evaporation intensity due to transfer of salt to surface layers is proven by experimental data on different solutions and materials [15]. To intensify subsurface crystallization requires increasing evaporation rate, therefore, the velocity of solution motion in capillaries of the mass according to Formula (1). In the tests this effect was gained by raising the temperature of a mass material up to 50-52°C with blowing of a warm air jet toward the mass surface. These parameters contribute to the growth up to 3–4 mm/h of the solution transition velocity to the surface; this is 5–10 times higher than the solution motion velocity under conventional test conditions. After a precipitate is formed and crystallized in the capillaries, the evaporation rate used to lower negligibly (Figure 3b). The crystals appear at the mass surface in 7 days, and their further growth remains intensive even after the feeding of the solution is canceled. In 10 days from the test launch, the most portion (80%) of salt fed to the column is found in a crystallized state.

It is apparent in Figure 3a that salt, crystallized from unconcentrated solution with no heating, distributes practically uniformly throughout the height of sand column. The effect of local concentrated salt cluster on subsurface aeration zone is not really detected. The growth of initial solution concentration conditions the precipitation of most portion of salt in the middle section of mass height. This effect may relate to the diffusion of solution in rock pores. Under the present experimental conditions at incomplete moisture saturation in pores in the middle section of column height, the diffusion of the solution declines, thus resulting in the growth of solution concentration in this section of the test mass. In tests with intensified evaporation distribution of precipitated nickel nitrate, salt appreciably differs by the zoning of precipitation. The highest concentration with high content of nickel and cobalt nitrates is detected at the surface of the test mass. **Figure 3b** presents the plot of zoning of nickel nitrate (2.75 Mol/l) distribution. The identical relationship is established for other solutions. It is established experimentally that the covering formed at the surface of the test mass is not regular, but with discrete crystal clusters (Figure 4). We suppose that it is mainly due to irregularities in the structure of a porous material. Pores distribute in a random manner, intercrossed; there

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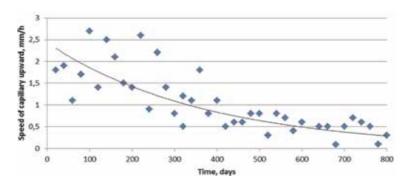


Figure 4. The rate of the filtration upward flow of the aqueous solution.

are blind pores with no outcrop to the surface. There are also through pores, providing prompt passage for the solution to the surface. Crystallization proceeds primarily nearby such pores. It is also found that in all the cases, including the intensified evaporation tests, salt used to crystallize in the mass periphery closer to the column walls (**Figure 3b**). Under the present test conditions, a threefold higher salt content is recorded in the periphery along the column walls as compared to the central experimental mass section. One of the reasons for this effect can be higher evaporation rate nearby column walls than that in the central section, thanks to higher solution motion velocity along the smooth column surface, confining the test mass. The established effect is in compliance with experimental data reported in [16]. A series of tests on measurement of intensity of the evaporation stream at the porous body surface revealed that at a rather small distance (about 2.5 mm) between porous material surface and an outlet of a hollow cylinder (that is correct for our tests), the evaporation stream is much higher in the periphery. In the tests with no heating, the evaporation stream is more homogenous at the surface with relatively uniform salt deposits (Figure 3a). The evaporation barrier in the aeration zone of mineral processing tailings serves as an integrated zone of valuable component accumulation under sustaining of "water mirror" at tailing mass and a directed ascending motion of solutions to the surface. The water evaporation from the surface contributes to the preliminary concentration of valuable components in the subsurface aeration zone of the tailing mass. The precipitation nature of watersoluble nickel and cobalt nitrates depends on how solutions pass the evaporation barrier. Distribution of nitrate concentration in the aeration zone depends on a solution motion velocity (evaporation rate). At low motion velocity, the evaporation zone develops in the depth of the mass displacing to the central section of the mass thanks to the decreasing diffusion of solution because the reduced humidity in the middle section of the mass height is compensated with inflow from more watersaturated lower section. This process results in the growth of solution concentration in lower and central sections of the mass aeration zone. The low solution motion velocity at indoor temperature and average humidity level does not provide the sharp zoning of salt crystallization. The salt crystallizes throughout the aeration zone with reduction in content from lower layers to the surface. This distribution is specific for both initial high- and low-concentrated solutions. As the moisturetransition rate increases, the evaporation area forms closer to the surface of the mass aeration zone, perhaps, due to the appearance of extra thermo-moistureconductivity phenomena. With the increase in evaporation intensity by heating or surface blowing, 61% of salt fed to the column tend to crystallize inside the mass pores starting from 7 to 10% from the surface, thus indicating the local higher nitrate concentration zone. It is established experimentally that it is possible to

control the processes of precipitation and crystallization of salts and to localize delivery of soluble salts to the mass surface with their respective lower concentration in the inner mass layers by regulating the intensity of solution motion in porous masses.

The capillary structure of massif has areas of "high-speed" pathways that allowed more rapid fluid flow and thus developed crystals more rapidly at their exit points on the surface. But instead of blocking evaporation at the pore, these crystals would boost the rate of evaporation by providing more surface area from which the fluid could evaporate. The increased evaporation would draw up fluid even faster along these high-speed pathways. In response, the flow through neighboring pathways would become slow, and the corresponding pores would be starved of salt. The salt crystallization in the salt mass on the surface forms capillaries commensurate with the capillaries of the soil. The height of the "salt mass" layer corresponds to the maximum height of the capillary rise of salt solutions with its own viscosity.

We have conducted experiments on the study of moisture transfer using media with different filtration characteristics: a layer of quartz sand and a layer of sand with a surface layer of hygroscopic material (microfiber). Investigated the suction effect of the material of the array above the boundary of the groundwater level. We studied the parameter of water capacity of a gyroscopic material with the aim of its possible use in calculations for production geotechnology. The influence of the hygroscopic layer on the surface of the changes in the kinetics of filtration and the groundwater level is established. The surface layer of a hygroscopic microfiber material increases the suction pressure by 100–250 mm and raises the water table by 40–45 mm.

Experimental evaluation is given for mineral preconcentration in a bed of a sorption collector in aeration zones from aqueous solutions of salts of low concentration useful components. Sorption collectors represented by interior layers of lignite, peat, marble, and vermiculite are included in an evaporation barrier installed in the subsurface zone of rock mass aeration in medium distance aeration zone in column (**Figure 1**). Migrating solution was aqueous solutions of salts of cobaltous and nickelous nitrates. The character of cobalt nitrate and nickel nitrate distribution is identical in all the tests. In view of this, the regularities of solely cobalt nitrate distribution are reported. Under conditions of bottom-up ascending of the test solution and its filtration through a marble sand layer, the distribution of cobalt nitrate content over the aeration zone height is close to linear and uniformly fading toward the surface (**Figure 3a**, curve 1).

Selective estimates of the influence of geochemical and sorption barriers on the kinetics and nature of the deposition of useful components in the indicated concentration zones were carried out experimentally. Layers of marble, vermiculite, brown coal, and peat were used in the aeration zone. The geochemical barrier made of a marble interlayer does not actually exhibit sorption properties and does not influence the character of cobalt nitrate distribution over the aeration zone height. In tests with bottom-up ascending of the solution through the aeration zone with the geochemical barrier made of lignite, the distribution of cobalt nitrate and nickel nitrate content is characterized with the increasing concentration of nitrates before the interlayer and nearby the upper boundary of lignite layer (Figure 5a, curve 2). The nitrate content linearly diminishes on the zone from the interlayer up to the surface. Cobalt nitrate content was not high at the surface of the column through the entire test. Lignite layer contributes to a partial reduction in cobalt content thanks to cobalt transition upward with ascending solution from lower layers. More than twofold rise of cobalt nitrate content was detected when the cobalt nitrate solution ascended through geochemical barrier made of Seibinsky peat (Figure 5b, curve 3). The higher cobalt nitrate content was recorded practically through the

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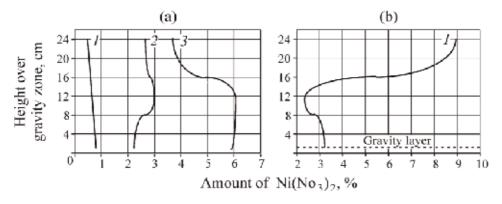


Figure 5.

Distribution of salt throughout the column height under different evaporation conditions: (a) $t = 22^{\circ}$; (1) 0.34 Mol/l; (2) 1.7 Mol/l; (3) 2.75 Mol/l; (b) $t = 52^{\circ}$, blowing rate 5–7 m/s.

whole peat layer. Humic acids are supposed to perform chemisorption concentration and provoke immobilization of cobalt nitrates in the form of complex compounds. Close-in-character cobalt nitrate distributions were obtained in the test with a geochemical barrier made of foamed vermiculite originated from Severny site of Low Angara area (**Figure 5b**, curve 4). A threefold increase in cobalt nitrate content was recorded in the sorption layer. In the background of neutral properties of vermiculite, the well-developed micro-, meso-, and macro-porosity of the interlayer material promotes concentration of cobalt nitrate in the layer. Velocities of solution motion in the aeration zone are closely related to atmosphere humidity (pair correlation factor $r \approx 0.8$ –0.9). The tendency to lower solution velocity 1 month later in a long-term test is traced. Variation in velocity of capillary ascending of the solution in the test with lignite interlayer is shown in **Figure 6**.

Investigation into the filtration of solutions through sorption collector being a component of the evaporating barrier in the aeration zone of the massif enabled to establish that in the course of ascending capillary lifting of the solution, the components redistributed with 1.5–3-fold concentration of cobalt nitrates in the neutral sorbent layer. The concentration in the sorption barrier does not depend on the sorption layer location in the aeration zone in the massif. In the tests with peat, the interlayers revealed feasibility to accumulate cobalt nitrate (nickel nitrate) from a solution with presumptive formation of a partially complex compound (approximately 10–12%). The sorption barrier made of marble with permeability, identical to permeability of the massif layer, does not actually generate the concentrating zone. Regularities of distribution in this case are similar to general regularities, specific for the evaporating barrier in the aeration zone. Sorption of cobalt and nickel nitrates in sorption barriers made of lignite and foamed vermiculite is not the

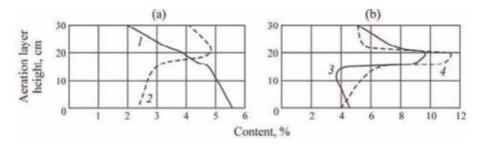


Figure 6.

Distribution of $Co(NO_3)_2$ content in aeration zone in the column with an interlayer: (a) (1) marble; (2) coal; (b) (3) peat; (4) vermiculite.

same. Nevertheless, their content in sorption layers exceeds two to three times nitrate content in the aeration zone free from sorption interlayers. The technological potential of sorption interlayers being a component of evaporating barriers of the aeration zone proves the reasonability to apply them as a preconcentration stage. Artificial sorption and evaporating barriers mounted in the way of solution motion make it possible to enrich the material of the sorption barrier with a valuable component with its feasible recovery in follow-up processing circuits. Application of sorption and geochemical barriers for the rising flow of fluids warranted performance deposition and accumulation of salts in the barriers.

4. Upward capillary leaching

The evaporation from the surface forms a capillary ascending rise of groundwater from the bowels. The groundwater contains water-soluble salts and passes by capillary flow through the aeration zone of the massif. When water evaporates into the atmosphere, all mineralization is retained and accumulates in the aeration zone and on the surface. This very powerful natural mechanism for solution flow through a column enables upward vertical movement due to the pressure gradient between the surface and the fluid level in the column. We see this mechanism as the main one for the formation of concentration zones on the surface of such man-made objects as tailing dumps. The water that evaporates from the solid surface into the atmosphere leads to the formation of this pressure gradient. The upward fluid flow rate is controlled by all the forces in the capillary system and the humidity. Water evaporation from the solution increases the concentrations of the useful mineral compounds along the direction of flow in the surface aeration zone. Here is a powerful natural method for the upward movement of solutions from the groundwater horizon to the surface. This very powerful natural mechanism for solution flow through a massif enables upward vertical movement due to the pressure gradient between the surface and the fluid level in this distance. Water evaporates from the solid surface into the atmosphere leads to the formation of this pressure gradient. The upward fluid flow rate is controlled by all the forces in the capillary system and the humidity. In agricultural areas, this phenomenon leads to harmful soil salinization. The lifting of salts in the solution to the surface and their deposition can be used in technological leaching solutions. This phenomenon has not yet been used in the leaching process and is just getting ready to become one. Solutions with a low concentration of salts are very mobile, have high fluidity, and are able to quickly move a useful component to the surface. They can move upward through the evaporation zone to the surface by capillary action. Water evaporation from the solution increases the concentrations of the useful mineral compounds along the direction of flow in the surface aeration zone. When these concentrations exceed the solubility limits, the useful compounds are deposited in the column. Different mineral compounds have different concentration limits in the solution; therefore, the compounds can be selectively precipitated at different heights in the aeration zone. Essentially, the aeration zone acts as a natural evaporation barrier. Selective enrichment can be achieved due to the physical nature of the capillary action in the upward direction and the deposition surface. Partial laws for the upward capillary rise of solutions were formulated in studies of agricultural soils. The soil particle size and stratification structure were shown to influence the capillary action considerably. To leach valuable compounds in situ, their velocity and the large contact surface area between the solution and solid material in the capillary system are important. These parameters must be optimized to ensure that the extraction is complete and the

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upward capillary leaching process can be controlled. For estimation of some main parameters, the laboratory experiments were made.

The tailing sample 5500 cm³ was placed in the cylindrical process column. The process solution was fed from below of the column; the solution was drinking water with pH \sim 7.0 and acid water with pH \sim 3.0 The column was equipped with branch tubes to sample the solution after filtration through different layers of solid phase (17, 40, 63 cm). The experiment was ran in two stages: water washing for 2.5 months and weak acid solution washing for same months. Daily, the contact solution was sampled, and chemical composition of the samples was analyzed using mass-spectrometer Agilent 7500 IGPMS. The content of Cu, Ni, Co, Fe, Mg, Pt, Pd, and Au was under control. Phase compositions of mineral forms were determined by geochemical analysis [10] of samples from the top, middle, and bottom layers of the process column. The initial geochemical analysis is presented in Figure 2. Mineralogical analysis of original material showed that the water-soluble forms made up the major part of the precious metals (31–46%), and the next largest was the part of crystal iron and manganese oxides (20-30%). Copper, nickel, and cobalt were in the form of sulfide minerals (43–61%); oxide phases were 13–27%. Exchange phases contained 4-10% of precious metals.

The test with drinking water for 2.5 months revealed that nonferrous and precious metals are prone to transit to a water-soluble exchangeable phase from the old tailing material. The transition of precious metals to the exchangeable phase runs no more intensively as compared to copper, nickel, and cobalt. Very weak partial dissolution of precious metals and their transition to the solution were established: gold and platinum up to 0.0006 mg/l and palladium up to 0.018 mg/l. The maximum content in the production solution was recorded for Au on the 5-7th days of activation, for Pt and Pd on the 2nd-3rd days with the further concentration decrease of the said components in the production solution. Redeposited mineral forms of precious metals contained water-soluble forms (9–17% gold and platinum, 5–8% palladium), iron oxide forms (26–53% platinum and 16–55% palladium), and organic matter forms (to 50% gold, to 17% platinum and palladium) as shown in Figure 1. Transfer of precious metals in the exchange form causes secondary geochemical processes when precious metals can go to amorphous oxides. That was observed experimentally: to 39% palladium and to 16% gold and platinum passed into amorphous oxides. Distribution of precious metals in the phase forms is different at different check levels heightwise the column of the tailings. For Pt in the top and middle layers, 50% are oxide forms, and the bottom layer is mainly carbonated. Pd oxide forms prevail in any layer. Gold from 31 to 50% is bound to organic matter forms and from 14 to 32%-to oxides. The water-washed nonferrous metal distribution in mineral forms is nearly identical in the tailings' column layers. There are almost no soluble forms, except for a few in the top layer (to 3%). In the middle and bottom layers, 54–71% nonferrous metals occur in sulfide and metal forms; in the top layer, there are few sulfides and more carbonates and sulfates (29–36%) and oxide phases (20-30%). There is low transfer of nonferrous metals to the exchange phase because these metals occur in the original material in weak-soluble forms of sulfide and oxides, which prevents from the redistribution. A low content of copper, cobalt, and nickel ions in the solution, mg/l: Cu up to 1.8, Co up to 0.11, and Ni up to 4.1, is explained by the fact that they are present in the initial material in the hardly soluble form as sulfides and oxides, thus hampering their redistribution. Migration capabilities of copper, nickel, and cobalt species are extremely low in an actually neutral aqueous medium. It is found that with the increase in time of percolation through a tailing layer, the content of copper, cobalt, and nickel tends to grow in the solution with the respective correlation versus iron content in the solution. This fact justifies the statement that nonferrous metals (copper and cobalt

in a greater degree and nickel in a less degree) are prone to adsorb onto iron compounds, for example, on its hydroxides (III), and to transit to the solution with decomposition of iron-containing minerals: pyrrhotite and chalcopyrite with the release of iron species into the solution. The acidity of the solution in the middle part of the column increased to $pH \sim 3.0$ after 2.5 weeks of filtration. At the top of the column, the acidity was close to normal ($pH \sim 6.0$) until the end of the third week. Geochemical phase analysis shows significant changes in the massif structure (**Figure 7**). This effect is due to water filtration. Phase transformations of mineral compounds in the bowels of the Earth are due to the occurrence of geological processes of hypergenesis. The geological natural process of hypergenesis in the presence of filtration does not stop, and even more than that, it proceeds more intensively than when there is no access of oxygen to the massif.

With an increase in the acidity of the medium, a more intense transition of nonferrous metals into the solution should be associated. Due to the effect of changing the acidity of the fluids during the supply of neutral water, experimental studies were carried out with the supply of initially weakly acidic water.

Pretreatment of the sampled material by acid solution to pH = 3 also changes the composition of nonferrous and precious metals subject to the thickness of the filtering layer. In this case, the correlation is direct unlike the first stage of the experiments. For thicker filtering layers, it is typical that the solutions have higher average values of the commercial mineral contents. The solutions sampled from layer 85.5 cm thick have nickel and cobalt contents 1.5 times higher than the solutions sampled from layer 40.5 cm in thickness. The platinum and gold contents change three times, while the copper and palladium contents are scarcely changed. The metal recovery in solution results obtained on the samples after the water washing and acid solution washing for 90 days is significantly different. The major portion (75%) of the soluble ion exchange forms of precious metals has gone to solution or redeposited in the epigenetic mineral forms. This share for nonferrous metals is 50–75%. Thus, water-soluble forms of nonferrous and precious metals are mobile, and their water leaching is quite feasible. The higher recovery is observed for gold (24%) and platinum (3.9%) in the filtering layer of tailings 85.5 cm thick, with the acid water pretreatment. Dissolution of the components with the weak acid solution is more intensive than with the water drink solution. The weak acid solution pretreatment improves copper, nickel, cobalt, and palladium recovery 4–9 times and platinum and gold recovery 500-4000 times. The analysis of redistribution of nonferrous and platinum group metals and gold in different mineral phases has confirmed the assumption on soluble forms of nonferrous and precious metals to appear in weathered aged tailings; some of the water-soluble forms go to solution and some redeposit as epigenetic minerals. Passing into solution intensifies in a weak acid solution with pH = 3. A weak acid solution forms independently in massif

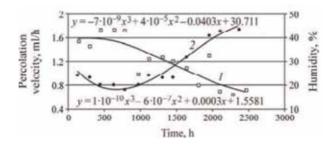


Figure 7.

Variations in velocity of $Co(NO_3)_2$ solution filtration with geochemical lignite barrier in terms of variations in atmosphere humidity during the test: (1) percolation velocity; (2) humidity.

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in the presence of crystalline and sulfide phase states in the original massif. Redistribution intensity of metal in mineral phases is different with different thickness of filtering layers and with different treatment solutions. After the water washing, epigenetic minerals contain precious metals in the form of organic compounds and iron oxide phases and a few soluble and ion exchange forms (9-17% gold and platinum, 5–8% palladium). After filtration of the weak acid solution, the amount of soluble forms remains the same, but metal passing into solution is higher. Passing of metals into solution correlates with the thickness of the filtering layer: under the water treatment, the thicker is the filtering layer, the less is the metal passing into the solution; under the weak acid solution treatment, the metal passing into solution is higher in the thicker filtering layer. The occurrence of soluble forms of precious metals inspires further research toward the creation of brand-new methods of commercial mineral recovery from processing waste. One of the methods may be the method of leaching by ecological nonaggressive solutions. The test experiments have shown recoverability of 28.4% gold and 3.9% platinum using the weak acid treatment solution. The water leaching approach requires smaller investment and is ecologically friendly. This research direction seems advisable.

Experimental studies with the upward movement of solutions in the array, at the water base, are aimed at carrying out a fundamental assessment of the technological applicability of direct concentration formation in the near-surface place of the massifs. The development option for the natural part of the field can be formed along the directions of concentration of mineralization on the surface of the massif, in the near-surface zone of the evaporation barrier, hygroscopic accumulation, and collection of the production solution from the surface area of the massif. In addition, there may be new approaches with geochemical and physical barriers to the upward capillary movement of solutions. The basis of such technological options for the extraction of useful components lies in the use of the hydrogeological natural resource of the Earth's interior.

Figure 8 shows the scheme of surface collection of the production solution with rising capillary filtration for an enrichment waste massif as a probable technological variant of the upward capillary lifting of the solution.

The content of useful components in the places of storage of the wastes is very low, and it is unprofitable to extract them by existing technology. The natural effect of the ascending capillary movement of fluids in the near-surface layer of the Earth's subsoil array allows preliminary selective concentration of useful and harmful components. When the zones of accumulated concentration of the useful component are created, the technology allows extracting profitably (**Figure 9**).

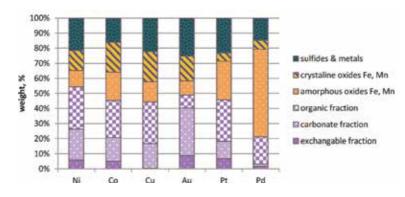


Figure 8. Geochemical phase analysis of the metals at the end of the experiment.

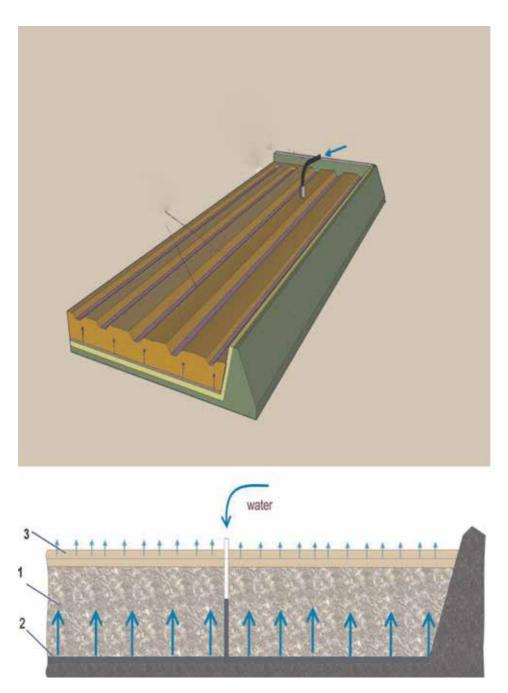


Figure 9.

Technological scheme for extracting useful components by water leaching and filtration lifting with surface collection of the production solution. (1) waste massif; (2) aquifer; (3) catchment surface channels (hygroscopic material).

5. Conclusion

The capillary leaching method is considered to be subsequently intensive and nontoxic to biota extraction of useful components. This way allows the subsequent intensive extraction of useful components. The mass exchange process in the capillary rise of hypergenesis carries out a gradual redeposition of the salts of nonferrous

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metals from the bottom up to the direction of movement of aqueous solutions. In such a way, the carried out experiment with water as a leaching agent for moving water-soluble compounds of nonferrous metals in the massif of flotation tailings shows that the geological processes of hypergenesis allow the leaching by water to conduct a directed preliminary concentration of nonferrous metals near the surface. The conducted simple experiments with enrichment waste materials for the entire test period allowed more than 70% of water-soluble nonferrous metal salts to rise to the surface. The concentration of nonferrous metals in the surface layer rose and exceeded the values of the existing conditions. So the content of Ni, Co, and Cu in the aeration layer amounted to 0.11, 0.09, and 0.07%, respectively. This way allows the subsequent intensive extraction of useful components. To accumulate useful components in close proximity to the surface of the array, both physical barriers (evaporation) and geochemical (sorption) barriers can be used.

The nonferrous metals are constantly present in the aqueous solution throughout the entire experiment. The concentration of the salts of nonferrous metals in the solution is not the same at different levels of the massif. In the initial period of the experiment, the trend of decreases of all elements of nonferrous metals in the solution from the bottom-up takes place. In the final period of the experimental cycle, the concentration of nonferrous metals in the upper zone exceeds the concentration of the lower zone by a factor of 2–4. The mass exchange process of hypergenesis carries out a gradual redeposition of the salts of nonferrous metals from the bottom-up in the direction of movement of aqueous solutions. The concentration of the zone of nonferrous metals shifts in the direction of movement of aqueous solutions in the array. After 1.5 years of experiment, the concentration of water-soluble compounds of nonferrous metals moved to the surface. Such results allow us to propose technological schemes for preparing the deposit for development. This approach to the development of deposits is suitable for natural deposits with a low subgrade content of useful components in the massif. Also, this approach is applicable to technogenic objects, such as wastes of enrichment and warehouses of substandard ores. The basic schemes are given in the materials of this article.

The such experiment with water as a leaching agent for moving water-soluble compounds of nonferrous metals in the massif of flotation tailings shows that the geological processes of hypergenesis allow the leaching by water to conduct a directed preliminary concentration of nonferrous metals near the surface. This way allows the subsequent intensive extraction of useful components. To accumulate useful components in close proximity to the surface of the array, both physical barriers (evaporation) and geochemical (sorption) barriers can be used.

The geochemical analysis of the material composition showed that the capillary water flow intensifies the process of hypergenesis and changes the ratio of the phase composition of nonferrous and noble metals. To the end of the experiment, the content of the sulfide phase is reduced by 80%, the carbonate phase is increased by 24%, and the oxide phase is increased by 41%. Such hypergene transformations increase the proportion of water-soluble salts and increase recovery by capillary leaching.

A more complete extraction of useful components from enrichment wastes will significantly reduce pollution of the groundwater and increase the natural attractiveness of the development territory.

The presented studies, which are quite simple, made the first step toward the development of a new technology for the cultivation of mineral deposits with the maximum use of natural processes for the transformation of the material composition in situ.

Salt in the Earth

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The Importance of Salt in Road Safety

Chapter 6

NaCl Material for Winter Maintenance and Its Environmental Effect

Ivana Durickovic

Abstract

All over the world, winter maintenance is based on the application of the NaCl salt on roads, a product necessary for the elimination of slippery conditions. The quantities used for the salting operations are increasing with the development of the road network (in France, up to 2 million tons are applied each winter). This chapter will present the salt used as a deicer (its origin and chemical composition) and its chemical properties that are exploited for that purpose. Furthermore, an overview of the means of its transfer from the roads to the environment (soils and waters) as well as its impacts on these media will be presented, a special attention being devoted to the soil. The interactions of salt with other road pollutants and the treatment possibilities in the road pollution context will be discussed.

Keywords: NaCl, winter maintenance, road salt, pollution, environmental media, environmental impacts, road runoff

1. Introduction

In order to ensure the road safety and accessibility during winter in cold regions, winter road maintenance operations need to be performed. These operations are mainly based on the application of chemicals on roads with specialized vehicles. Large quantities of the so-called road salts, or deicing salts, are thus applied in order to clear the pavement and allow the normal traffic flow and economic activity [1].

Road salt was first introduced for snow melting operations in the 1930s [2], in order to improve vehicle traction [3] and thus reduce automobile collisions [4]. Sodium chloride (NaCl) has been the most commonly used deicing agent since the late 1940s [5, 6]. Application of road salts has been shown to reduce automobile accidents by 88% and human injuries due to icy conditions by 85% [7].

According to various climatic characteristics, urban environments, economy, and life requirements, people in different regions have different requirements for the consumptions of chlorine deicing salt [8, 9]. Improved management practices and regulations have resulted in reduced road salt application in some regions [4, 10]. However, the amount of deicing salt spread during cold periods increased since the 1940s [5, 11], but more particularly during the 1960s with the increasing road and highway network [12–14] and when its usage became widespread for highway maintenance [2]. For instance, the quantities applied in the USA increased from 149,000 tons in 1940 to over 18 million tons in 2005 [11]. Hence, this led the transportation

officials to yearly apply approximately 17 million tons in the United States, 6 million tons in Canada [7], up to 2 million tons of NaCl in France [15], and 600,000 tons in China [16]. The precise amounts of road salt applied are difficult to quantify [17], especially when it comes to road salts applied by individual land owners and other private entities. Kelly et al. [4] estimated that up to 40% of deicing salt application in some areas may be from private users [8].

Once spread on roads, due to several meteorological conditions and traffic, the road salt is transported out of the roads into the surrounding environment [10]. Another part remains on the road surface until the humidity coming from the precipitations or from the ice/snow melting is sufficient for flows of a road runoff [12]. In order to diminish the direct transfers of road runoffs to the environment, treatment systems, such as retention ponds, are constructed alongside roads [13, 18]. However, these ponds treating the pollutants only by sedimentation, dissolved pollutants, such as sodium chloride, will only pass through the pond and be rejected into the environment at its output [5, 18].

Severe impacts related to road salt applications have been reported on water and soil, as well as on their vegetation and population. Significant increases in chloride and sodium concentrations in surface water, groundwater, roadside soils, and organisms have been reported and were correlated to deicing salt application [19–21]. Indeed, salt stress can reduce the utilization rate of water in soil, cause water shortage, and even cause plant death in severe cases [22]. Different soil types and plants suffered different degrees of deicing salt damage [23, 24]. In some cases, concentrations have even reached toxicity thresholds beginning to threaten biodiversity [25, 26]. Moreover, salt has indirect environmental impacts, as Na⁺ and Cl⁻ ions are known to remobilize heavy metals adsorbed on the particle surface (soils and sludge) [27].

Despite the increasing use and concerns about the environmental impacts of road salt, only a few countries regulated the quantities spread on roads or developed a specific treatment for wastewaters contaminated by sodium chloride [28]. Canada, on the other hand, has much more drastic regulation declaring deicing salts as toxic products and limiting their use [29].

2. Salting operations

During winter conditions, certain meteorological phenomena lead to slippery conditions that provoke a decrease of the friction between the vehicle tires and the road surface [30], thus representing a risk for traffic. Thus, the transportation officials have the responsibility to ensure the winter road maintenance, which encompasses all the actions and decisions aiming to fight the consequences of winter phenomena on the road network necessary in order to maintain the viability and safety of road users. Snow and ice control can be made with mechanical or chemical methods [31]. Mechanical methods for the removal of snow, ice, or frost from the road surface consist of scraping or pushing [1]. These methods are mainly used on the mountain roads, where the thickness of the accumulated snow on the roads is too large [32]. Chemical treatment, based on the use of road salts, is the method used in a large number of countries of Europe, Africa, Asia, and the USA. Numerous road salts exist: chlorides of sodium, magnesium, or calcium, alcohols (methanol, ethanol, and ethylene glycol), acetates of potassium or sodium, and formates of potassium or sodium [33]. The salt selection depends not only on the local climate and legislation [9] but also on the surface that needs to be treated. Hence, for more sensitive zones, less corrosive acetates and formates are employed [34].

For the road treatment, on the other hand, sodium chloride is the most preferred anti-icing compound, and is thus used in the largest quantities. It has been widely selected because of its low cost, high availability, easy use and storage, and high efficiency up to a temperature of approximately $-8^{\circ}C$ [2, 5, 31].

2.1 Origin and composition of sodium chloride as a road salt

Sodium chloride used as road salt can come from different sources. The main types are sea salt (produced by natural evaporation of sea water) and rock salt (salt mechanically extracted from underground deposits) (**Figure 1**), but the new European standard includes other possible origins: ignigenic salt (obtained by recrystallization of brine produced by injection of water into the salt layers), salt of second intention (coproduct or industrial waste revalued), and brine of natural sodium chloride or produced from the dissolution of salt in water [35].

Besides the origin, road salt has to fulfill requirements stated in the European standard also in terms of granularity, humidity, pH, and composition (proportion of chlorides, soluble sulfates, heavy metals, insolubles, and anti-caking agents).

Road salt is mainly composed of its so-called active compound (sodium chloride), but it also contains insolubles and impurities such as metallic trace elements, whose quantity and nature vary as a function of the salt origin [12, 36]. Furthermore, other substances may be added for better efficiencies, such as anti-caking agents [2].

As an example, the composition of the rock salt extracted from the Varangéville mine, the only mine extracting rock salt for winter maintenance in France, is presented in **Table 1**.

2.2 Principles of operation of road salt

Deicing salt is a product whose physical and chemical characteristics permit to move the equilibrium of water phases in order to lower the freezing point. Under atmospheric pressure, pure water will have a freezing point at 0°C, and beneath that temperature, it will be in its solid form and will form ice on the road surface. It is possible to decrease the freezing point by the addition and dissolution of a solute, such as salt, in water (**Figure 2**). Thus, the formed aqueous solution is called brine when the solute is sodium chloride.



Figure 1.

Stocks of sea salt coming from the Aigues-Mortes in the Occitanie region of France (left) and of rock salt coming from the Varangéville mine in the Lorraine region of France (right).

Solubles (mass % on dry)		Insolubles (mass %)	
Cl⁻	56.4	Silicates	90
SO4 ²⁻	0.86	Carbonates	5
Br ⁻	0.01	Sulfates	5
Na⁺	36.6		
Ca ²⁺	0.36		
Mg ²⁺	0.02		
K ⁺	0.09		
Fe(Cn ₆)Na ₄ , 10H ₂ O: 114 mg/kg			

Table 1.

Composition of a sample of rock salt from the Varangéville mine [37].

A brine can be characterized by its so-called weight percentage, that is, the ratio between the mass of the salt dissolved and the mass of the solution. As shown in the NaCl-H₂O phase diagram presented in **Figure 2**, a brine's freezing point decreases with the concentration increase until the eutectic point, which corresponds to a weight percentage of 23.31 and a freezing point at -21° C. For temperatures lower than -21° C, a sodium chloride dihydrate, NaCl * 2H₂O, is formed.

The NaCl-H₂O phase diagram permits to identify the role of the salt diluted in water. Indeed, if we concentrate on what happens at -5° C, we can see that for low concentrations, the solution will be composed of ice and liquid. A part of the solution being frozen, there is danger of appearance of slippery conditions. However, for higher concentrations (weight percentage above 10%), the solution will be entirely liquid.

In winter maintenance context, rock salt applied on ice will captivate free water, forming a brine. When the thus formed brine's freezing point becomes lower than the surrounding temperature, the fusion of ice or snow will start, diminishing the presence of the solid phase. The efficiency of the deicing salt to melt ice will depend on its concentration, the quantity of water present (from

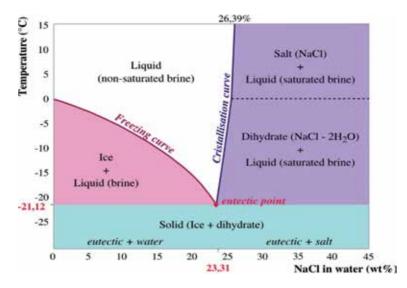


Figure 2. NaCl- H_2O phase diagram [37].

precipitations, air humidity, or water on the road surface), as well as on the temperature [38].

Depending on the state of the road, deicing salt can be spread as [12, 31]:

- dry salt: method convenient for very wet periods,
- in solution as a brine: efficient at dry conditions as it adheres to the surface, even though the brine can be easily drained off,
- moistured/humidified salt (mixture of a 30 wt% brine and of rock salt): efficient in numerous situations, as the dry salt will be the salt stock and ensures a mechanical effect, whereas the brine will bring the humidity necessary for the fusion.

The application can be performed either before the appearance of slippery conditions (preventive salt spreading) or once they are present on the road surface (curative salt spreading). With its capacity to lower the freezing point of the liquid present at the road surface, road salt prevents the formation of ice or provokes its melting.

3. Transfers of salt to the environment and its environmental impacts

Numerous parameters and mechanisms lead the salt to be transported out of the roads into the environment. When deposited on soils, it can either be retained by the soil or infiltrate and percolate to groundwater [6, 31].

This represents a real environmental issue since NaCl is known to have adverse environmental impacts [5]. Indeed, besides increasing the salinity in soil and water, salt may induce a range of other effects [39]. First of all, it increases the hardness of water, provokes acidification of receiving waters [40], and strongly influences water geochemistry by the ion mobility, more specifically of metallic ions, *via* ionic exchanges and complexation with chlorides [20, 41–43]. Secondly, it can be retained onto soils and increase ionic strength and pH, thus modifying ion speciation [41, 44], but may also lead to alteration of the soil structure [31]. As a result, the disintegration of soil aggregates and increased mobilization of colloids can lead to a transport of heavy metals from soil to groundwater [27, 39]. And finally, in high concentrations, NaCl causes stress to ecosystems, decreasing biomass development and increasing mortality of species and therefore causing a modification of the biotope [45–48].

3.1 Transfers

Any salt spread eventually ends up being in some part of the environment [2]. After their application on roads, road salt will be submitted to numerous parameters, such as meteorological conditions (precipitations and wind) and traffic [23, 49], which will influence its evolution. Most of this salt is removed through drainage (after precipitations or snow/ice melting) [3, 8] or traffic spray processes which will transfer it to the adjacent roadside environment [2]. The main transfer mechanisms, such as runoff, infiltration, airborne spreading, and plowing, are represented in **Figure 3**.

The transfers to the different environmental compartments will take place in the first hours following the salting operations [31]. First of all, it is estimated that 20–40% of the totality of rock salt spread is directly projected out of the roads during the salting operation [15]. Blomqvist and Johansson [31] stated that 20–63% of road salt is transported by air (projected by vehicles and wind).

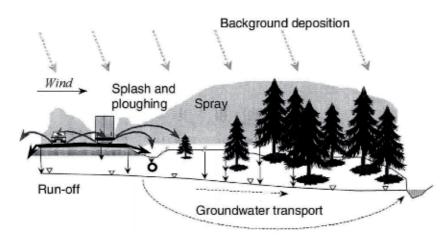


Figure 3. A conceptual model of the transport mechanisms and pathways from the road [10].

The NaCl dissolved in storm water can be transferred in two ways. Firstly, it is projected out of the roads by nebulization. The distance to which road salt is transferred by nebulization can reach 400 m [50], even though more than 90% is found within 20 m from the road [31] and 98% within 50 m of the road edge [14]. Secondly, the runoff containing dissolved salt can be collected in retention ponds. These systems can collect between 40 and 80% of the totality of the road salt applied, depending on the meteorological conditions [12] and have the role of improving water quality and reducing flooding risks. Retention ponds allow the reduction of metallic pollution by decantation of suspended solids bearing trace elements, but in general, they are not designed to treat dissolved pollutants like NaCl [5]. Since sodium chloride is not removed by the retention ponds, after passing through those systems, road salt is rejected into the environment. There is thus a lack of appropriate storm water management practices [6].

It is found that up to 50% of the applied road salt reaches surface waters [6, 51, 52]. The remaining 50% enters the subsurface as aquifer recharge and migrates toward groundwater [6, 46, 53].

Further transfers will depend on the nature of the elements that are deposited, as the salt will be dissociated into sodium and chloride. On the one hand, chloride is considered to be a conservative element as it does not participate in chemical reactions. It will therefore follow the water and be transported down to the groundwater, from where it can be further transported to other groundwater aquifers or to various surface waters. Sodium, on the other hand, takes part in chemical processes, such as cation exchanges, with soil particles and is therefore retained in the soil [39, 54].

3.2 Impacts on waters

Concentrations of Na⁺ and Cl⁻ increase in superficial and underground waters during winter, following the salting operations [14, 20, 36, 42, 43, 55–61]. Due to long retention times of these ions by soils and waters, this increase can continue during the summer period [56] and high concentrations in lakes and underground waters can be observed during several years [36, 42, 57].

Increased chloride concentrations in groundwater or surface waters because of deicing salt application are the first observable change in water quality and indicate that there is a hydraulic connection between the road and the water [39].

3.2.1 Underground waters

Road runoff reaches underground waters by infiltration in soils [62]. Salt concentration of underground waters varies with the quality of soil or from 1 year to another. The increase of the salting operations leads to an increase in the salt concentration of shallow ground waters [53–55]. The concentrations of Na⁺ and Cl⁻ ions present in underground waters were also correlated with the permeable surface fraction which can receive road salt [46].

Aquifers play a role of reservoir wells for NaCl during winter [62], and become a source during summer, rejecting salted waters in the streams, thus contaminating surface waters [42, 54].

3.2.2 Surface waters

Road runoff presents very high Cl^- concentrations during winter, leading to salinity increase and water quality degradation [20, 36, 40, 58, 63]. In suburban and urban streams of Maryland, chloride concentrations can achieve 5 g/L [20] and the lakes of Minneapolis receiving waters charged in road salt have Na⁺ and Cl⁻ concentrations 10–25 times greater [36].

The impacts of road salt on surface water can be physical, chemical, or biological: change of lake density stratification, eutrophication, mobilization of metals, reduced diversity, and so on [58].

In France, the Luitel Lake (Isère) is a remarkable example of the road salt influence on surface waters. Indeed, the winter Olympic Games organized in 1968 at Grenoble led to the emergence of winter sport resorts and the development of the road network to access it. The Luitel bog, located upstream and below a department road leading to the Chamrousse resort, suffered the consequences of this development, with an important increase of Na⁺ and Cl⁻ concentrations since 1968: chloride concentration measured in 1955 was 3.7 mg/L, 34 mg/L in 1982, and 49 mg/L in 1999 [15]. A change in the lake's aquatic population was later observed [64]. Another example is the Saint-Augustin Lake in Québec where an unexpected presence of some brackish water and marine samples appeared in the second half of the twentieth century. This was identified as a result of the increasingly saline conditions from road and highway saltings [21].

The residence time will determine the evolution of Na⁺ and Cl⁻ concentrations. If the residence time is lower than a year, these concentrations will diminish before the next winter season, forming annual cycles [36, 65]. If the residence time is longer, Na⁺ and Cl⁻ will not be flushed completely between salting seasons and will still be present in waters next winter, leading to a gradual increase of these concentrations from 1 year to another [62]. Hence, Kelly et al. [42] observed the increase of Cl⁻ and Na⁺ concentration in rural streams of New York of 1.5 and 0.9 mg/L, respectively.

The salinity increase in waters was correlated to the increase of Mg^{2+} , K^+ , and Ca^{2+} cation concentrations coming from soil road runoff passed through [66, 67]. Judd et al. [68] attributed the Ca^{2+} and K^+ concentration increase in the Third Sister lake (Michigan) between 1981 and 2004, to cationic exchanges between those ions and sodium, whereas concentrations of Mg^{2+} and SO_4^{2-} remained unchanged.

Lakes present stratification with a temperature and density gradient, the superficial layer being warmer. In autumn, as the air temperature decreases, it induces convection streams leading to a homogenization of the water column permitting the brewing of nutrients and dissolved oxygen. In winter, the presence of ice on the lake surface leads to a stratification reversal, the surface layer becoming colder than the lower layer. At spring, air warming inverses the process [69].

Salt in the Earth

The income of dissolved NaCl induces a modification of the thermal stratification in favor of a chemical stratification. Waters charged in NaCl, denser, are located in depths [70]. This chemical stratification prevents the brewing of water masses, with eutrophication risks [36].

3.3 Impacts on soils

After being deposited on the ground, road salt infiltrates the soil and is further transported down the soil profile to eventually reach the groundwater [39]. Despite the runoff and storm drains, one part of salt is accumulated in soil [23]. Hence, Howard and Haynes [51] estimated that only 45% of the chlorides were removed annually by surface runoff in Toronto (Canada), the rest of it remaining in soil water or ground water.

3.3.1 Cation speciation

It was observed that Ca and Mg are present in higher concentrations in soils in the vicinity of roads [23, 40, 41]. Indeed, after salting operations, Na⁺ concentration increases in the soil solution. Sodium enters in competition with other cations at the sites of ionic exchanges leading to an increase in Mg²⁺ and Ca²⁺ concentrations in the soil solution [19, 41, 56, 61, 63, 66, 71–75]. Because of its stronger attraction to negatively charged soil particles, Mg²⁺ may accelerate Na⁺ leaching by displacing it in soils [23]. Thus, faster movement of Na⁺ through soils make Na⁺ less available to plants, but more available to aquatic systems [23].

Sodium can also enhance the release of metals from soils to groundwater [19, 23, 27, 76]. Hence, increased transport of heavy metals (Zn, Cd, Cu and Pb) coincident with road salt applications has been observed in roadside soils in Germany, Sweden, and the United States [36].

Due to their physicochemical properties, metallic trace elements have different speciations according to the pH and chemical environment. Metallic trace elements with weak solubilities fix on preferential phases that vary according to physicochemical conditions on the water-solid interface. Metals such as Cu and Cd have strong affinities for organic matter and are present in aqueous phases in the form of chloride complexes. Other metal, such as Pb, Cr, and Zn have a strong affinity for organic matter that influences their mobility in the presence of Na⁺ and Cl⁻. Li et al. [77] showed that in a soil of a nontreated road, Pb and Zn were present mainly in the phases of carbonates and oxides of Fe and Mn, whereas Cu was mainly associated to organic fractions and to sulfides. Durand et al. [78] observed in sediments of retention ponds that Cd, Pb, and Zn were linked to fulvic acids and were mobile, while Ni and Cr were mainly present in the humic fraction and were thus little mobile. Pb and Zn can also precipitate as oxides [76], while Cd forms chloride complexes in the presence of dissolved NaCl [74].

3.3.2 Impacts on the soil quality

Several anthropogenic factors disturb the state of urban soil by changing its natural features and internal processes [79]. Geomechanical transformations are often accompanied by chemical changes. The accumulation of different pollutants and their subsequent synergetic and antagonistic reactions lead to an increasing level of toxicity in urban soil [80]. One of the observed changes is the salinification of urban soils, a side effect of salting the roads in winter, which will lead to a physicochemical modification of the soil and influence the mobility of metallic trace elements.

Soils in the vicinity of roads present higher concentration of metals and road salts. As an example, the first 20 cm of depth next to main roads in Opole (Poland), chloride concentration can go up to 1.5 g/kg [79].

Road salt accumulation in soils depends on several parameters: the soil permeability and its density, and its mechanical properties influence the salt transport and the physicochemical processes. The Na⁺ and Cl⁻ ions can be retained in soils next to rural and urban roads in Missouri for 2–3 months after the end of the salting period, namely in soils containing organic matter, such as sandy soils [61]. According to Lundmark and Olofsson [81], soils with coarse particle size, which are more permeable, will have greater salt leaching down the soil profile.

More conservative Cl⁻ is less retained by soils [2], leading to concentrations in water higher by 10–15% than the Na⁺ concentration [40]. However, several studies showed that chlorides can be retained in forest soils [82], as well as rural soils [83]. Indeed, the chloride ion can interact with the organic matter in order to form chlorinated organic complexes and be stocked in soil micropores [40, 56, 82, 84]. Besides acting like a well, soil is also a source by liberation mechanisms with Cl⁻ and Na⁺ ions interacting with the soil components [82, 84]. The ions are then leached toward underground waters or transported to surface waters.

Numerous lixiviation tests showed the capacity of NaCl to remobilize metallic trace elements. The alternation of leaching with rainwater charged in Na⁺ and Cl⁻ and water with weak ionic force promotes the release of colloids formed of carbonates, clay, and organic matter [27, 72, 74, 85]. Moreover, the presence of Na⁺ and Cl⁻ leads to a competition for the sorption sites [63]. Metallic trace elements are easily leached in the presence of NaCl [19, 27, 72, 74, 76, 85] and can be transported by the soil solution toward surface or underground water.

Salinization is a threat for soils, mainly in arid countries where irrigation is performed with salted waters [12]. Clays can contain in their structure Ca²⁺ ions that permit to obtain structures presenting little swelling or dispersion. Conversely, the presence of Na⁺ in clays induces the formation of a platelet structure, more mobile in interstitial water. The presence of Na⁺ in the soil provokes particle (clay and organic matter) dispersions [66] and a swelling decreasing hydraulic conductivity by obstruction of pores [86, 87]. Structural stability of a soil, apparent density, and soil permeability will then decrease in the presence of Na⁺ [86–89]. Colloids are evacuated during the leaching of soils by salty waters [72, 74]. The soils presenting high salinities induce a release of Ca, Mg, and K.

3.3.3 Impacts on the vegetation

Once in the roadside environment, salt may percolate downward into the soil and become available to plant roots or the underlying water table or be deposited directly on roadside vegetation [79]. Many authors have shown a direct correlation between the content of Na⁺ and Cl⁻ ions in the soil and the degree of plant damage [22, 90]. Indeed, increases in Na⁺ concentration tend to leach out K, Ca, and Mg cations, which can result in nutrient deficiencies in certain soil types [24, 72]. The higher the concentration of Na⁺ and Cl⁻ ions in the soil, the higher their accumulation in plants and, consequently, the greater the damage to plants [79].

The most significant symptoms of salts on roadside trees are growth limitation/reduction in biomass, necrosis, defoliation, and in extreme cases, the entire destruction of a plant [12, 49, 79]. These symptoms can be caused by several salt effects: photosynthesis reduction, decrease of soil moisture, decrease of water content in leaf tissues, alteration of nutrient availability, etc. [24]. It is estimated that the use of road salt is responsible for the death of 700,000 trees/year in Western Europe [91] (**Figure 4**).



Figure 4. *Roadside vegetation impacted by road salt* [92].

A good example of the impact of urban runoff on biota is the Frenchman's Bay lagoon, receiving direct runoff from Canada's busiest highway. Eyles et al. [53] underlined a marked reduction in the area of vegetation of a wetland corresponding to 30% since 1970 and 60% since 1939. Furthermore, reduced diversity and coverage of submergent plant species is reflected in changing fish populations in the lagoon. The authors showed that the largest contemporary impactor on environmental quality in Frenchman's Bay watershed derives from the salting operations.

4. Treatment possibilities

Contaminated soils and waters can be remediated by various methods which are not suitable for an *in situ* treatment. For the road runoff treatment, conventional desalination techniques (reverse osmosis and membrane processes) are too expensive.

Currently, preference is being given to *in situ* methods that are less environmentally disruptive and more economical. In this context, biotechnology offers phytoremediation techniques as a suitable alternative [93].

Phytoremediation is based on the use of plants and their associated microorganisms for the removal, degradation, or stabilization of toxic substances from the environment. Depending on the contaminant and on the plant characteristics, different phytoremediation techniques take place (**Figure 5**).

The first objective of the phytoremediation is to limit the impacts of some contaminants. This can be obtained by several ways. Firstly, by phytostabilization, that is, immobilization of the contaminant in the contaminated soils (after incorporation of contaminants into roots, metals are precipitated as insoluble forms and trapped in the soil matrix). This technique diminishes the mobility and bioavailability of contaminants by different mechanisms such as sorption, complexation, or precipitation [94]. Secondly, by phytodegradation of the contaminant (contaminants are degraded inside plant cells by specific enzymes) [93, 95]. And finally, by phytoextraction from the soil which involves the absorption of contaminants by roots and their accumulation in the aerial parts [96]. It is mainly applied to metals (Cd, Ni, Cu, Zn, and Pb) and preferentially uses hyperaccumulator plants that have the ability to store high concentrations of specific metals in their aerial parts (0.01–1% dry weight, depending on the metal). Phytoextraction is the most commonly used technique and probably the most economic and efficient one [94].

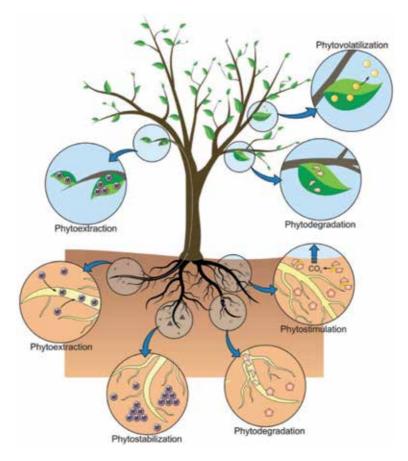


Figure 5. Schematic representation of phytoremediation strategies [93].

In order to develop such a technique for the remediation of a contaminated soil, it is important to choose appropriate plants. Indeed, the choice of the plant will depend on the environmental conditions it will be submitted to, mainly soil composition and pollutant that is aimed for phytoremediation. In order for a plant to be considered as a good phytoremediator, it has to have high tolerance to the pollutants and has to be able to accumulate or degrade pollutants. For a good efficiency, it is necessary that the plant has fast growth and high biomass production, as well as a well-developed root system. Finally, it has to be well adapted on the climatic and environmental conditions it will be submitted to [18].

Phytodesalination, in particular, is a modality of phytoextraction based on the use of halophytes for removal of salts from saline soils. Several studies investigate the possibility of using phytodesalination for road runoff treatment [97–102].

Morteau et al. [100] investigated a possibility for the treatment of road runoff in Québec by *Atriplex patula*, *Salicornia europaea*, and *Spergularia canadensis*. The authors showed that all species accumulated important masses of salt, but that the mass of accumulated salt depends on the plant morphology (size and weight), species, and concentration of the salt exposure. Their study shows that, taking into account the chloride accumulation and plant weight, *Atriplex patula* is the most suitable for the accumulation of chlorides and of sodium.

Suaire et al. [102] and Durickovic et al. [97] showed that two Atriplex species (*Atriplex hortensis* and *Atriplex halimus*) seem to be well adapted for the road runoff remediation. Indeed, these species showed they both have salt and metal

accumulation abilities, but also have capacities suited for the implementation in the road runoff treatment systems. Indeed, *Atriplex hortensis* is particularly interesting because of its fast growth rate, attending 1 m of height in 1 year and *Atriplex halimus* because of its water stress tolerance and ability to accumulate metals, contaminants that are also present in road runoffs.

5. Conclusion

Significant increases in sodium and chloride concentrations in the different environmental compartments (water, soil, and biota) have been reported and correlated to deicing salt application. These increases lead to important environmental impacts such as the increase in soil pH and salinity, modification of the soil structure, reduction of the availability of nutriments for the vegetation, and loss of biodiversity. Hence, many European countries (Germany, Finland, Norway, Sweden, and Switzerland) and Canada are preoccupied with the environmental risks that the usage of deicing salt implies. They entered the usage of deicing salts in their code of the environment and prohibited their use in vulnerable areas. Canada also entered road salt in their list of toxic products of the Canadian law for the protection of the environment in 1999.

Despite of its well-known environmental impacts, it is not possible to overcome the need of usage of salt as road salt. Numerous studies are led in order to optimize its applications and diminish its rejections into the environment. However, even if the quantities applied on roads are diminished, the salt will nevertheless end in the environment.

The concentrations of sodium and chlorides rejected into the environment may only be regulated by controlling the water output flow of collection systems or retention ponds along roadside. Several studies investigate the possibility of using phytodesalination (i.e., extraction of salt from soil or water by plants which concentrate it in their biomass) for road runoff treatment. These studies show promising results, particularly with the *Atriplex* halophytes species, but are still in their research phase and are not yet operational. In the meantime, salt surveillance in environmental media is thus of great importance in order to identify the areas that are most vulnerable and where optimization of salting operations, as well as of retention systems are needed.

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Salt is a predominant compound for humankind and the earth preserves an important source of this element of life. This book reviews this multi-disciplinary issue in which geoscientists, historians, agriculturalists, medical doctors, and general scientists have been interested in its nature. The authors have provided contributions on the origin and history of salt, intrusion with freshwater effect, its usability as a material, and its role in life. The safety of groundwater resources should be a priority for humanity. Contribution on this important topic is provided by geophysical investigations to characterize saltwater intrusions in aquifers. This book also presents a general overview on salt intake and its role in food and human health. Methods of salt recovery and surface salination as well as its usage in the environment will provide new aspects in earth science.

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