Recovery of Rare Earth Elements from coal fly ash by nanofiltration

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I am happy for having shared this long trip with old and new friends, always close to me in the happy and more stressful moments of these years.
Abstract

Rare earth elements (REEs) are critical and strategic materials in a wide range of applications required for the development of future green economy. Coal combustion fly ash has been proposed as alternative REEs source considering their content and ease of extractability by hydrometallurgical acid leaching. However, potential technologies for REEs recovery from acid leachate, their performance and economic feasibility are uncertain. The objective of this study was to optimize a nanofiltration REEs recovery process maximizing its economic feasibility. Nanofiltration (NF) pre-treatments, such as pH adjustment and microfiltration, have been optimized enhancing REEs purity in the NF feed. In order to assess the simultaneous effects of the operating conditions (NF feed pH and applied pressure) on the NF rejection and permeate flux, 42 cross-flow NF experiments have been carried out according to two experimental design plans and testing four commercial nanofiltration membranes using pre-treated synthetic leachate. Response surface methodology was used to model experimental flux and REEs rejection data obtained from different values of NF feed pH (1.5, 2.5 and 3.5) and applied pressure (12, 18 and 24 bar). REEs rejection was improved increasing the feed pH and decreasing the applied pressure. The opposite trend was found for permeate flux, enhanced by pH decrease and pressure increase. Analysis on membrane fouling suggested that flux decline and membrane fouling increased together with pH and ions rejection. To optimize the NF operating conditions, an economic model was developed, where capital and operating costs were estimated for pre-treatments, NF and post-treatment steps, as well as the recovered REEs sale returns. The optimum operating condition combination was found to be at pressure 12 bar and pH 3.5 which gave the highest REE rejection (99.3%) and the lowest permeate flux (15.9 LMH). The estimated REE recovered mass resulted in a specific gain of 0.275 $/kg_{ash}$. The performance of NF in the optimal operating conditions was further investigated with real leachate, showing a different performance due to the diverse ions concentrations.
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Introduction

Rare earth elements (REEs) are critical and strategic materials in a wide range of applications including key technologies developed to provide sustainable mobility and energy supply. Their “criticality” is a measure that combines importance to clean energy economy, relation between supply and demand and risk of supply disruption. The REEs availability appears to be at risk not only because of the increasing demand exceeding the production capability, but also because China, with more than 86% of global REEs production, has steadily increased their export taxes, drastically restricting their export quotas in recent years. Since United States highly depend on REEs import, the U.S. Department of Energy outlined the need for alternative REEs sources as a required strategy for the development of future green economy. Coal ash has been investigated as potential alternative source of REEs due to its abundance, resulting from the production of one-third of the U.S. electricity from coal, and the economic and environmental issues generated by its disposal. Previous studies have shown that many coal deposits around the world contain high REE levels, and the respective ashes are also enriched in REEs. The major focus thus far in the research literature has been on the total REEs content in coal ash and their extractability with hydrometallurgical techniques, in which REEs are leached from fly ash by acid extraction. However, the economic feasibility of REEs recovery from coal ash is uncertain. More attention is needed to develop scalable, high-efficiency REEs recovery processes, to be applied to the leachate produced by acid extraction, and to make coal fly ash an economically feasible and environmentally sustainable REEs alternative source. REEs are present in the acid leachate as trivalent cations. Although previous studies have successfully applied nanofiltration (NF) process to separate multivalent ions from aqueous solutions, also in acidic conditions, none of these investigations focused on REEs.

For these reasons, the present research activity aims at optimizing the nanofiltration process for REEs recovery from the acid leachate, assessing its economic feasibility. To achieve this goal, a first literature review has been performed to understand the nanofiltration separation mechanisms, the major parameters describing its performance and the operating conditions influencing it. In addition, economic models, provided in literature to assess nanofiltration feasibility, have been analyzed.

In the second part of the study, a first set of experiments has been carried out on a synthetic leachate, at laboratory scale, to optimize the pre-treatment steps needed before the nanofiltration step. Secondly, nanofiltration tests have been conducted to evaluate its performance in terms of permeability and REEs rejection. In particular, the
The following nanofiltration design parameters have been optimized: NF membrane, applied pressure and feed solution pH. The nanofiltration experiments were performed in accordance to experimental plans based on the statistical method of the Design of Experiments (DoE). This method has allowed to evaluate the effect that each design parameter and possible interactions between two parameters have on the NF performance. The data resulting from the experiments have been used to develop two performance models for the nanofiltration process. The NF process optimization has been based on its economic feasibility, assessed using a cost model developed integrating the experimental performance models to already existing cost models. Further tests have been performed with the optimized pre-treatment and nanofiltration configuration on real acid leachate. Furthermore, the effects of the kind of leachate and the NF feed pH on NF membrane fouling has been evaluated.

The present study has been carried out in collaboration between Politecnico di Milano and Duke University. It has been performed during a 6-month period of international mobility, funded by Politecnico, at Duke University. This study is inserted in the project “Novel membrane and electrodeposition-based separation and recovery of Rare Earth Elements from coal combustion residues”, briefly described in Chapter 1.
Chapter 1 - Project description

This study, aimed at optimizing REEs recovery by nanofiltration and assessing its economic feasibility, is inserted in the project “Novel membrane and electrodeposition-based separation and recovery of Rare Earth Elements from coal combustion residues”. This research project is the result of the collaboration of three universities (Duke, Yale and Kentucky Universities) and the Research Triangle Institute (RTI, North Carolina). It is supported by the U.S. Department of Energy Office of Fossil Energy (Award#DE-FE0026952). In addition, research for the preliminary data was supported by the National Science Foundation programs in Environmental Engineering (CBET-1510965) and Partnerships in International Research and Education (OISE-12-43433).

The goal of the project is to develop a bench-scale system to recover Rare Earth Elements from coal fly ash and other coal combustion residues (CCRs). The proposed general approach, as shown in Figure 1.1, involves hydrometallurgical techniques, in which REEs are leached from fly ash by acid extraction and further separated from the leachates by membrane filtration and electrochemical deposition.

Specifically, this project has been divided among the investigators to:
- identify and characterize a representative selection of CCR samples as candidates for REE recovery (University of Kentucky: James Hower, expert in coal ash geochemistry);
- evaluate the efficiency of acid extraction techniques as a function of CCR extraction conditions (Duke University: Helen Hsu-Kim, expert in aquatic geochemistry);
- optimize membrane filtration (Duke University: Mark Wiesner, expert in membrane separation) and carbon nanotube-enabled electrochemical deposition techniques (Yale University: Desiree Plata, expert in environmental nanotechnology) for concentration of REEs from CCR extracts;
- perform a technical and economic feasibility study of the proposed separation methods (Research Triangle Institute International, Zachary Hendren);
- develop an implementation plan for a bench-scale system.
Chapter 2 - Background and literature review

This chapter is divided in four sections. Chapter 2.1 presents an overview on geochemical characteristics, sources and market of the Rare Earth Elements (REEs). In chapter 2.2, the REEs’ recovery techniques are illustrated. Chapter 2.3 focuses on nanofiltration (NF) separation mechanisms, the main factors affecting NF performance and the cost models describing its feasibility. Lastly, in chapter 2.4, an introduction about the DoE methodology and its application to NF studies is presented.

2.1. Rare Earth Elements (REEs)

The International Union of Pure and Applied Chemistry (IUPAC) defines the Rare Earth Elements as a group of 16 elements consisting of 14 lanthanoids [La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu] plus Scandium [Sc] and Yttrium [Y] (Alonso et al., 2012). The REEs are lithophile elements (elements enriched in the earth’s crust) that invariably occur together naturally because all are trivalent and have similar ionic radii. The similar radii and oxidation states of the REEs allow for liberal substitution of the REEs for each other into various crystal lattices (Castor et al., 2006). This substitution accounts for their wide dispersion in the earth’s crust, with total REE average crustal content between 160 and 205 mg kg⁻¹. However, REEs are not found in nature as pure metals and must be isolated from the host minerals, where they also do not occur as individual constituents due to their chemical similarity (Taggart et al., 2016). There are approximately 200 distinct rare earth minerals, but of these only bastnaesite, monazite, xenotime, and ion-adsorbed clays are mined for commercial REEs production (Kanazawa et al., 2006). The chemical and physical differences that exist within the REEs group are caused by small differences in ionic radius and allow their classification into three geochemically diverse groups: light earth elements (LREE: La, Ce, Pr, Nd and Sm), medium (MREE: Eu, Gd, Tb, Dy and Y) and heavy (HREE: Ho, Er, Tm, Yb and Lu) (Blissett et al., 2014). REEs demand and supply trends over the years and the issues resulting from the instable market are explained in Chapter 2.1.1. Chapter 2.1.2 focuses on coal fly ash as REEs alternative source.

2.1.1. REEs applications and market trends

The Rare Earth Elements are interesting for different applications because they are characterized by the following properties, listed by Hocquard et al. (2010):
- Chemical: unique electron configuration;
- Catalytic: oxygen storage and release;
- Magnetic: high magnetic anisotropy and large magnetic moment;
- Optical: fluorescence and high refractive index;
- Electrical: high conductivity;
- Metallurgical: efficient hydrogen storage in rare earths alloys.

The commercial importance of REEs is not reflected in the amount in which they are used, but in the fact that they provide critical functionality in a wide range of applications including key technologies developed to provide sustainable mobility and energy supply. Hocquard et al. (2010), Humphries et al. (2012) and Alonso et al. (2012) reported the major applications of REEs in different industry sectors, summarized in Table 2.1.

**Table 2.1.** Rare Earth Elements major industry sector and end-use applications.

<table>
<thead>
<tr>
<th>Industry Sector</th>
<th>End use</th>
<th>REEs</th>
</tr>
</thead>
</table>
| Magnets               | • NdFeB permanent magnets [Hard Disk Drive (HDD), optical and acoustic devices]  
                          • Miniaturization of electrical and electronic components [audio and video, computers]  
                          • Wind turbines  
                          • Vehicles [hybrid, electric, plug-in]  | Nd; Pr; Dy; Gd; Tb    |
| Battery Alloy         | • Ni-(La)-MH Battery for hybrid vehicles, HEV, single cell, cordless phone     | La; Ce; Nd; Pr; Sm    |
| Metal Alloy           | • Alloying agents in Al, Mg, Fe, Ni, Steel Alloys  
                          • Pyrophoric alloys  | Ce; La; Nd; Pr       |
| Autocatalysts         | • Automotive catalytic converters for diesel particle elimination  
                          • De-sulfurization catalysts  
                          • Chemical and polymerization catalysts  | Ce; La; Pr; Nd       |
| Petroleum Refining    | • Fluid Cracking Catalysts (FCC)  | La; Ce               |
| Polishing Compound    | • Glass Polishing Powder  
                          • ‘Nano’ Powder  | Ce; La; Pr           |
| Glass additives       | • UV cut glass screen  | Ce; La; Nd; Y; Pr    |
| Phosphors             | • Low consumption lamp [fluorescent light, LED]  
                          • Flat screen display [plasma and LCD]  
                          • Medical radiography  | Y; La; Nd; Ce; Pr    |
| Ceramics              | • Ceramic capacitors  
                          • Oxygen sensors  | Ce; Y; La; Nd; Pr; Sm; Gd |

A basic scenario, described by Alonso et al. (2012), uses historical trends (2006-2010) as a predictor of future trends in REEs markets with a disaggregated evolutionary demand growth rate for each industry sector. The resulting sectorial demand trends (in tons of REEs) until 2035 are reported in Figure 2.1, with the fractional REE demand.
Figure 2.1. Evolution of market distribution of REE demand: Total (left) and individual REE market share (right) (Alonso et al., 2012).

Figure 2.1 shows that this scenario, modeling demand for REE growing at an overall rate of 5.3%, would correspond to an approximate doubling of demand between 2010 and 2025. The REEs demand in 2035 is estimated to be more than 3.5 times the one in 2010. The changes to the REE portfolio are modest, with small increases in Nd, Pr, and Dy and small decreases in Y, Sm, and Gd demand (Alonso et al., 2012).

To deeply understand the reasons behind the increasing concern about REEs availability, it is important to add to the demand trend over the years also an evaluation of their supply. Kingsnorth (2009) estimated the relationship between the production and consumption of individual REE in the next five years at retention of current tendencies in industrial development. Results are reported in Table 2.2. Seredin (2010) used the resulting estimation to classify the REEs based on their “criticality”. For this purpose, “criticality” is a measure that combines importance to the clean energy economy, the relation between supply and demand for each element and risk of supply disruption.

Table 2.2. Forecast (accuracy ±15%) of global production and consumption of individual REE (oxides, kt) in 2014 (Kingsnorth, 2009).

<table>
<thead>
<tr>
<th>REE₂O₃</th>
<th>Production</th>
<th>Demand</th>
<th>Difference</th>
<th>Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>La</td>
<td>55.10</td>
<td>51.05</td>
<td>4.05</td>
<td>1.08</td>
</tr>
<tr>
<td>Ce</td>
<td>82.40</td>
<td>65.75</td>
<td>16.65</td>
<td>1.25</td>
</tr>
<tr>
<td>Pr</td>
<td>10.00</td>
<td>7.90</td>
<td>2.10</td>
<td>1.27</td>
</tr>
<tr>
<td>Nd</td>
<td>33.30</td>
<td>34.90</td>
<td>-1.60</td>
<td>0.95</td>
</tr>
<tr>
<td>Sm</td>
<td>4.00</td>
<td>1.39</td>
<td>2.61</td>
<td>2.88</td>
</tr>
<tr>
<td>Eu</td>
<td>0.90</td>
<td>0.84</td>
<td>0.06</td>
<td>1.07</td>
</tr>
<tr>
<td>Gd</td>
<td>3.15</td>
<td>2.30</td>
<td>0.85</td>
<td>1.37</td>
</tr>
<tr>
<td>Tb</td>
<td>0.40</td>
<td>0.59</td>
<td>-0.19</td>
<td>0.68</td>
</tr>
<tr>
<td>Dy</td>
<td>1.80</td>
<td>2.04</td>
<td>-0.24</td>
<td>0.88</td>
</tr>
<tr>
<td>Y</td>
<td>11.65</td>
<td>12.10</td>
<td>-0.45</td>
<td>0.96</td>
</tr>
<tr>
<td>Er</td>
<td>1.00</td>
<td>0.94</td>
<td>0.06</td>
<td>1.06</td>
</tr>
<tr>
<td>Ho+Tm+Yb+Lu</td>
<td>1.30</td>
<td>0.20</td>
<td>1.10</td>
<td>6.50</td>
</tr>
<tr>
<td>Total</td>
<td>205.40</td>
<td>180.20</td>
<td>25.20</td>
<td>1.14</td>
</tr>
</tbody>
</table>
According to this estimate, the demand for Nd, Tb, Dy, and Y exceeds their output. Keeping in mind the accuracy of the forecast performed by Kingnorth, Seredin states that it cannot be ruled out that Eu and Er will fall into the critical group. Thus, these six elements, which belong to both LREE and HREE in any classifications, should be regarded as critical REEs (Seredin, 2010). At the same time, Ce, Ho, Tm, Yb and Lu have been defined excessive due to their higher production compared to the industrial consumption. The rest of REEs (La, Pr, Sm, Gd) with a relative balance between production and consumption, have been classified as uncritical. Naturally, this classification makes an evaluation of the REEs distribution more relevant to the industry, compared to the geochemical one (Franus et al., 2015). The relation of the two classifications is illustrated in Figure 2.2, showing the percentage of each REE to the total reserves.

![Figure 2.2. Percentage share of various REE in total REE composition of the Upper Continental Crust and their classifications (Seredin et al., 2012).](image)

This figure shows the importance of considering market and not geochemical characteristics as a basis for REEs classification, since they provide different groups subdivision. Furthermore, it underlines the need to combine supply and consumption rates, to evaluate which REE's availability must be considered of concern. In fact, there are some critical REEs (e.g. Nd) with higher concentration in the upper continental crust than some of the excessive REEs (e.g. Yb).
REE resources are not that rare, since deposits have been identified in 34 countries according to Chen (2011), but because their mining and production are not cheap and can be associated with significant environmental impact, most of world’s countries, including the United States, highly depend on their import (Massari et al., 2013). The REEs availability appears to be at risk not only because their individual mining is economically inefficient, since they are found together in geological deposits, or due to the increasing demand exceeding the production capability. In fact, the main concern is due to the Chinese monopoly on REEs market with more than 86% of REE production, nearly half of known reserves, and the majority of REE processing and separation (Taggart et al., 2016). The REEs production trends for China, United States (USA) and other countries, including Australia, India, Brazil, Kyrgyzstan, Sri Lanka, Russia, Malaysia and Thailand, are shown in Figure 2.3.

![Figure 2.3](image)

**Figure 2.3.** Production of Rare Earth Elements by China, USA and other countries from 1950 to 2014 (Mech-chem Ass, 2014).

With its monopoly, China progressively increased export taxes on them and restricted their export rates (a decrease of about 40% between 2009 and 2010) (Massari et al., 2013) pressuring high-tech manufacturers to relocate and elaborate their products in China (Hocquard, 2010).

**2.1.2. Coal fly ash as alternative source of REEs**

As there is a gap between REEs’ growing demand and supply and due to recent instabilities in the REEs global supply market, the U.S. Department of Energy (DOE) outlined in a technical document (Bauer et al., 2010) the need to implement three strategies with respect to critical materials, such as REEs. First, diversified global
supply chains with multiple sources of materials are essential to manage availability risk. This means, in one hand, taking steps to facilitate extraction, processing and manufacturing in the United States in an environmentally sound manner and, on the other hand, the need for alternative sources, especially for critical elements such as Nd, Eu, Tb, Dy, Y, and Er. Secondly, substitutes must be developed. Research leading to material and technology substitutes will improve flexibility and help meet the material needs of the clean energy economy. Third, recycling, reuse and more efficient use could significantly lower world demand for newly extracted materials.

The need for alternative REE sources, underlined by the US DoE as a required strategy for the development of future green economy, led to a new research area focused on the investigation into coal ash as potential alternative sources of REEs. In fact, it seems to attract more and more attention and investment since almost one-third of U.S. electricity is produced from coal (U.S. EIA, 2017). The U.S. electricity production from coal generates annually approximately 115 million tons of coal combustion products (CCPs), including 53 million tons of fly ash. A coal combustion process for electricity production with its flue gas treatment line and generated CCPs is shown in Figure 2.4.

**Figure 2.4.** Coal combustion and flue gas treatment line scheme (Taggart et al., 2016).

Coal combustion residues are a major economic and environmental burden due to their abundance and potential to leach toxic metals at disposal sites. Although there is a number of possible applications in concrete and other construction materials, only 43% of fly ash (23 million t) are reused (American Coal Ash Association, 2015). The residues are considered a pollutant and disposed of as waste in landfills or wet impoundments where the leaching of toxic trace elements (e.g., As, Se, Cr) is a concern for groundwater, surface water and soil quality (Blissett et al., 2012; Taggart et al., 2016). As a consequence, the heavy economic and environmental costs associated with disposal have renewed efforts to find beneficial reuse opportunities that extend the value chain for coal ash. Although there are many publications regarding fly ash
utilization and there is precedent for metal (gallium, germanium and aluminum) recovery from fly ash, there are only few studies looking into its potential as REEs resource (Franus, 2015).

The recovery of REEs from fly ash has several advantages over traditional REE ores. First, it is a readily available waste product with strong environmental incentives and an established market for beneficial reuse. Second, REEs extraction process from fly ash is considered far less intensive than mining a raw product. In fact, fly ash does not require extensive excavation, which is capital intensive and can be environmentally destructive. REEs mines can generate large volumes of radioactive waste rock with high contents of uranium and thorium (Taggart et al., 2016). In addition, coal fly ashes contain a full range of REEs, whereas most mines have only a few varieties of these elements (Franus, 2015). Finally, several costly ore processing steps can be replaced by chemical processing, that is ideal for a fine powder as fly ash (Mayfield, 2013).

While there are potential advantages, the economic feasibility of REEs recovery from coal ash is uncertain. This is due to a lack of information on the REEs contents of the different types of coal ash produced across the U.S. and how ash characteristics are related to extractability of the REEs. In particular, it has to be established how ash composition impacts on the extraction and recovery processes selected and their efficiencies.

Previous studies have shown that many coal deposits around the world contain high REEs levels, and the respective ashes are also enriched in REEs. The average REEs content of world and U.S. coals is estimated to be respectively 68.5 mg kg⁻¹ (Ketris and Yudovich, 2009) and 62.1 mg kg⁻¹ (Finkelman, 1993), about 2.5 times lower than that in the rocks of the upper continental crust (UCC) (168.4 mg kg⁻¹; Taylor and McLennan, 1985). The average REEs content in world (404 mg kg⁻¹) and USA (517 mg kg⁻¹) coal ashes is approximately 2.5-3 times higher than that in the UCC. Mardon et al. (2004) revealed REEs contents between 1965 and 4198 mg kg⁻¹ (ash basis) in the Kentucky Fire Clay coal samples and 1200 to 1670 mg kg⁻¹ in fly ash from a power plant burning this coal source. Seredin and Dai (2012) found REEs contents of up to 1290 mg kg⁻¹ in the Pavlovka coal deposit (Russian Far East), with up to 1% REE in the resulting ash. Taggart et al. (2016) found average total REEs content for ashes derived from Appalachian sources of 591 mg kg⁻¹ and significantly greater than in ashes from Illinois and Powder River basin coals (403 and 337 mg kg⁻¹, respectively). Furthermore, the fraction of critical REEs (Nd, Eu, Tb, Dy, Y and Er) in the fly ashes was 34–38% of the total and considerably higher than in conventional ores (typically less than 15%) (Taggart et al., 2016).
The major focus thus far in the research literature has been on the total REEs content while the ease of extractability may matter more than that. More attention is needed to develop scalable, high-efficiency extraction and recovery processes to make coal fly ash an economically feasible and environmentally sustainable REEs alternative source.

### 2.2. REEs recovery techniques

Critical metals from coal ash are generally extracted by a first hydrometallurgical method involving dissolution and solvent extraction, such as a leaching step to dissolve REEs out of fly ash. This process is used at the industrial scale for extraction of REEs and other metals from ore particles and generally involve nitric acid (HNO₃), sulfuric acid (H₂SO₄), or hydrochloric acid (HCl). This technic is among the most powerful to separate and purify REEs (Turgis et al., 2016).

Neumann Systems uses by-products of scrubbing emissions, that is sulphuric and nitric acids, for the extraction process, with an additional environmental benefit (Currie, 2012). This system successfully extracts more than 60% of the available metals (including 14 REEs and strategic metals) from fly ash samples supplied by a Colorado Springs Utilities power plant. Taggart (2016) experimented a nitric acid-extraction with a percentage recovery for all the ashes, except for the Powder River Basin ashes, lower than 44.1% even though heat (85–90 °C) and concentrated (∼15 M) HNO₃ were used. Powder River Basin ashes had the highest extractable REE content, with 70% of the total REE recovered by heated nitric acid.

Further processes are required to concentrate, purify and separate REEs from the acid leachate solution, where they are present as trivalent cations. These processes might need to be tailored specifically to the type of fly ash (Taggart et al., 2016). Membrane-based strategies have been proposed for concentrating metals, including REEs. Some of these processes have been widely applied for other purposes such as water and wastewater treatment.

Pressure driven processes such as reverse osmosis (RO) and nanofiltration (NF) have been evaluated as capable of concentrating ionic species, such REEs in the acidic extraction solutions. For example, Murthy (2010) successfully optimized the separation of Pr(III) from aqueous solutions by nanofiltration.

Another strategy is to complex metals into a micelle phase that is then separated using lower-pressure ultrafiltration (UF) membranes. To achieve metal removal, micelles are formed using an anionic surfactant. Metals migrate into the micelle and are complexed by negative functional groups. The micelles are separated from the fluids by the UF membrane, and then the micelle is broken to recover the metals and the surfactant.
Micelle-enhanced ultrafiltration (MEUF) has been used to treat metal-bearing wastewaters for the removal of Cd$^{2+}$, Zn$^{2+}$, Cu$^{2+}$, Cr$^{3+}$, and other metals (Huang et al., 2010; Bade et al., 2011). A scheme of the MEUF process is reported in Figure 2.5.

![Figure 2.5](image)

**Figure 2.5.** Micelle enhanced UF scheme for haloacetate removal (Roach et al., 2013).

Hasan et al. (2009) modeled Gd recovery from nitrate medium by liquid emulsion membrane (LEM). In this configuration, an organic membrane phase, consisting of an immiscible organic solvent with an extracting agent and an emulsifier, envelops aqueous phase droplets of a stripping agent. These are present as a stable emulsion within the aqueous feed solution containing the metals to be extracted. After allowing sufficient contact time for the metals to be transported across the liquid membrane and enter the stripping solution, the emulsion is separated from the feed using a microporous membrane. Hasan et al. illustrated the process scheme shown in Figure 2.6.

![Figure 2.6](image)

**Figure 2.6.** Mechanism of metal ion transport through the LEM (Hasan et al., 2009).
A variation on the LEM is to place an immiscible solvent containing an extracting agent in contact with the feed solution via a microporous hydrophobic membrane. In this configuration, the microporous membrane serves only as a support for the liquid extractant. A solution of the stripping agent is then used on the concentrated extractant solution to remove the concentrated metals and regenerate the stripping solution for reuse. This process (supported liquid membrane, SLM, extraction) has been demonstrated for the recovery of Pr, Sm and Y (Gaikward et al., 2003). Gaikward et al. illustrated the process with the scheme shown in Figure 2.7.

**Figure 2.7.** Illustration of metal ion transport in extraction and stripping bulk liquid membrane (Gaikward et al., 2003).

### 2.3. Nanofiltration

This chapter provides an overview on nanofiltration (NF) membrane process focusing on its separation mechanisms (Chapter 2.3.1), its performance and the main factors affecting it (Chapter 2.3.2) and the cost models used to assess its feasibility (Chapter 2.3.3).

#### 2.3.1. Nanofiltration separation mechanisms

Pressure driven membrane filtration is a separation process, which utilizes a semipermeable membrane barrier to separate chemical compounds from feed solution to permeate and retentate streams. Nanofiltration is the most recently developed pressure-driven membrane process for liquid-phase separations. The properties of NF membranes lie between those of non-porous RO membranes, where transport is governed by a solution-diffusion mechanism, and porous ultrafiltration (UF)
membranes, where separation is usually assumed to be due to size exclusion (Chaabane et al. 2004). Figure 2.8 presents pressure driven membrane filtration processes, typical pore sizes and compounds that membranes retentates.

![Figure 2.8](image.png)

**Figure 2.8.** Pressure driven membrane processes, with estimated pore sizes and example compounds which can be retained.

Nanofiltration possesses the potential of high degree of multivalent ions separation at relatively lower operating pressure (typically 7 to 30 bar) and permitting higher fluxes than reverse osmosis and significantly better rejection than ultrafiltration. Lower energy consumption, pumping and membrane cost compared to those of reverse osmosis membranes often make nanofiltration a more economically and operationally attractive option (Chakrabortty et al., 2013).

The NF separation mechanism can be identified as a sum of convection and diffusion transport mechanisms, sieving effects, together with electromigration as a result of membrane charge, in addition to the Donnan potential developed at the interface as a result of ion distribution (Carvalho et al., 2011). Convective transport of ions with the water flux through the membrane is caused by the pressure difference between feed and permeate sides. Similarly, diffusive transport is a consequence of the concentration gradient as achieved by the rejection of solutes. Electromigration is caused by a “streaming potential” difference across the membrane. This streaming potential is caused by the electric current generated by the convective flow of a fluid that is necessarily charged through the pores of a charged membrane (Artug, 2007). For uncharged molecules, sieving or size exclusion is primarily responsible for separation and it is controlled by molecular size in solute form. Ion separation by nanofiltration membranes may exploit both steric (sieving) mechanism of UF and Donnan (electrical) mechanism of RO (Bowen et al., 2002).

Synthetic membranes can be manufactured from large variety of materials such as polymers, ceramics, glass, metals and liquids. Nanofiltration commonly utilizes
polymeric composite membranes with homogeneous skin layer also known as thin film composite membranes (TFC). The TFC membranes are asymmetrical membranes which consists from ultrathin top layer and two additional sub layers, that are a porous support layer and a non-woven backing layer. The top layer is typically manufactured from crosslinked aromatic polyamides (PA), although other formulations, such as polyvinylidene fluoride, polyethylenimine and polyethersulfone (PES) composites, have also been formulated and found to be effective (Park et al., 2012). The top layer of a membrane is typically the selective barrier where molecular rejection occurs as a result of the surface charge developed by dissociation of surface groups such as sulphonated or carboxyl acids (Shon et al., 2013).

The retention of ions mostly depends on ion concentration, valence and chemical nature of components along with membrane composition, surface charge and charge density (Dey et al., 2012). The membrane with a strong charge (higher charge density) produces a greater repulsive force than one with a weak charge (Bartels et al., 2005). As function of the surface charge, due to electrostatic repulsion positively charged membranes theoretically reject multivalent cation much better than monovalent cations and attract multivalent anions more strongly than monovalent anions. Figure 2.9 illustrates the surface charge and its density effect on ions rejection for a negatively charged membrane.

![Figure 2.9. Donnan potential created by the repulsion of anions and attraction of cations by a strong (left) and weak (right) negatively charged membrane (Bartels et al., 2005).](image)

The size of pores in NF membranes (nominally ~ 1 nm) and the surface electrostatic properties allow monovalent ions to be reasonably well transmitted with multivalent ions mostly retained (Bowen et al., 2002). These characteristics make NF membranes extremely useful in the fractionation and selective removal of solutes from complex process streams, separating ions with different valences (Shon et al., 2013).

Due to its separation capabilities, nanofiltration has found wide applications in many industries such as recovery of dye from textile effluent (Viero et al., 2002), treatment of paper mill process water (Manttari et al., 2002), removal of color from industrial waste
water (Frank et al., 2002), separation and removal of heavy metals in soil operations (Volchek et al., 2002) and metal recovery from wastewater (Fane et al., 1992). NF membranes can remove hardness, organics and particulate contaminants from water, thus it can be used to treat all kinds of water including groundwater (Van den Bruggen et al., 1998), surface water (Koyuncu et al., 2001) and wastewater (Afonso et al., 2001). In addition, NF is used as a pretreatment in desalination processes to lower the required operational pressure in sea water RO plants (Potie et al., 2003).

Nanofiltration could be utilized efficiently also in metal processing industry to separate metal ions from acidic waste streams (Katselnik et al., 1998) and for treatment of metal-bearing acid mine wastes (Zhong et al., 2007). In copper cathode manufacturing, nanofiltration is utilized to remove harmful multivalent ions such as manganese and iron while simultaneously increasing copper concentration in leaching liquor. Nanofiltration can be even used in processes which contain high concentration of strong acids (Schaefer et al., 2005).

Typically, in industrial applications each membrane housing consists from multiple spiral wound modules. Spiral wound (SW) module is a cross-flow filtration module which is rotated around itself providing a leaf like geometry. In cross-flow filtration the feed stream is directed tangentially across the membrane surface. The module consists from permeate spacer which is covered on both sides with membranes and feed spacers. The module structure is designed to enable two-sided mass transfer trough membranes into the permeate spacer. The feed spacer on the contrary is designed to enhance mass transfer near membrane (SWMF, 2016). The downside of spiral wound modules is high pressure loss along the membrane leaf. Due to their inherent design SW membrane modules are prone to fouling along membrane leaf and difficult to clean. Thus, SW membrane systems are typically expected to require advanced pre-treatments (Sethi et al., 2000). Figure 2.10 presents the structure of spiral wound membrane module.

![Figure 2.10. Structure of spiral wound membrane module (SWMF, 2016).](image)
2.3.2. Nanofiltration performance modeling

NF separation is industrially implemented, and it is generally considered as proven technology. However, despite the extensive use of NF, the mechanism of transport through NF membranes has not been yet completely explored in detail. At a fundamental level, NF is a very complex process (Kovacs, 2008). NF models are intended to obtain permeate composition as a function of feed composition and operating conditions. Several models have been proposed for NF so far. Most of these models were based on the extended Nernst-Planck equation (Equation 2.1), that is the basic equation to describe the transport of ions/solutes through the membranes (Chaabane et al., 2004).

\[
J = D_p \frac{dc}{dx} - \frac{zcD_p}{RT} F \frac{d\psi}{dx} + K_c c V
\]

where:
- \( J \) = ion flux based on membrane area (mol m\(^{-2}\) s\(^{-1}\));
- \( D_p \) = hindered diffusivity (m\(^2\) s\(^{-1}\));
- \( c \) = ion concentration in the membrane (mol m\(^{-3}\));
- \( x \) = distance from the membrane (m);
- \( z \) = valence of ion;
- \( R \) = gas constant (J mol\(^{-1}\) K\(^{-1}\));
- \( T \) = absolute temperature (K);
- \( F \) = faraday constant (C mol\(^{-1}\));
- \( K_c \) = hindrance factor for conversion;
- \( \psi \) = potential difference;
- \( V \) = solvent velocity (m s\(^{-1}\)).

The terms on the right side of the Equation 2.1 represent transport of solutes due to diffusion, electric gradient, and convention respectively. Thus, the equation can predict solute rejection as a function of feed concentration, ion charge, convection across the membrane, and solute diffusion (Braghetta, 1995). Different authors used the extended Nernst-Planck equation to model the transport through NF membrane of monovalent or bivalent single electrolytes, such as NaCl, KCl, Ca\(^{2+}\), Mg\(^{2+}\), H\(_2\)AsO\(_4\)\(^{-}\), F\(^{-}\), SO\(_4\)\(^{2-}\) (Bowen et al., 2002; Chaabane et al., 2004; Gozálvez-Zafrilla et al., 2008; Pal et al., 2012; Chakrabortty et al., 2013).

As for all current descriptions of NF, the modelling approaches are more descriptive than truly predictive due to the utilization of empirical fitting parameters. Despite the
considerable progress in the development of transport models, at present, it is difficult to accurately predict the performance of NF membranes when complex solutions consisting of more solutes are to be processed. As a result, currently piloting is highly recommended for NF applications (Kovacs, 2008).

Important aspects to be studied regarding nanofiltration performance can be roughly divided into flux through the membrane (solvent permeability) and retention of solutes (Li et al., 2008).

According to Spiegler and Kedem (1966), the volume permeate flux, $J_v$, can be expressed by Equation 2.2:

$$J_v = L_p \left( \Delta P - \sigma \Delta \pi \right)$$  \hspace{1cm} (2.2)

where:
- $L_p$: solution hydraulic permeability (L m$^{-2}$ h$^{-1}$ bar$^{-1}$)
- $\Delta P$: applied pressure (bar)
- $\sigma$: reflection coefficient
- $\Delta \pi$: osmotic pressure difference (bar)

The osmotic pressure difference, $\Delta \pi$, can be calculated based on the Van’t Hoff law reported in Equation 2.3.

$$\Delta \pi = RT \left( \sum C_{fi} - \sum C_{pi} \right)$$  \hspace{1cm} (2.3)

Where $C_{fi}$ and $C_{pi}$ are the ions concentrations at the membrane wall and in the permeate, respectively, shown in Figure 2.11.

![Figure 2.11. Solute concentration profiles in the membrane and the feed boundary layer (Gozálvez-Zafrilla et al., 2008).](image)
Since the flux depends on the osmotic effect caused by the salt concentrations at the membrane wall, the ability to predict rejection and flux simultaneously further improves the prediction capability (Mohammad et al., 2003).

The rejection is defined as:

\[
Rej_i = 1 - \frac{Cp_i}{Cf_i}
\]  

(2.4)

where \(Cp\) and \(Cf\) represent, respectively, the solute concentrations in the permeate and feed streams.

The main effects of some operating conditions and feed solution characteristics on the membrane performance, in terms of flux and ion rejection, are briefly described.

**Applied pressure**

Applied pressure is the main factor affecting the membrane permeate flux, as reported in Equation 1.2: permeate flux increases linearly with applied pressure.

The pressure effect on ions rejection is highly dependent on the solution to be treated. Lee et al. (2014) found that an increase in pressure led to a decrease in phosphorous rejection. He states that when the operating pressure increased beyond a certain limit, in this case 10 bar, drag forces dominated over the surface forces, resulting in a decrease in rejection. Abidi et al. (2016) studied the selective retention of phosphate from synthetic solutions and found that it increases with pressure at first, then stabilizes and eventually reduces. In Aydiner et al. study (2010) a high tartrazine rejection of approximately 98% was obtained for both low and high values of transmembrane pressure, from 12 to 24 bar, slightly decreasing with pressure, due to more transport of dye into the membrane.

**Feed solution ion concentration**

The feed solution ionic concentration has an important effect on the NF membrane performance in terms of permeate flux. In fact, an increase in ionic concentration at the membrane wall results in a higher osmotic pressure, as in Equation 2.3, and a consequent decrease of the permeate flux, according to Equation 2.2.

A further flux decrease is due to the ability of membranes to reject particles, colloids, solutes and ions, that result in a phenomenon called fouling. Fouling is a long-term flux decline which is caused by accumulation or adsorption of foulant material on membrane surface or inside the membrane matrix, that is enhanced by higher feed
solution ionic concentration. This is shown by Fang et al. (2013) in Figure 2.12, where the increasing concentration of feed SiO2 results in a lower permeate flux over time.

![Figure 2.12. Relative flux as a function of time with SiO2 at three different concentrations [base line: 30 mg/l; 135 mg/l; 405 mg/l] for the nanofiltration membrane (Fang et al., 2013).](image)

Pretreatment is emerging as the most promising solution to control the fouling and the potential mechanical and chemical damages as it is simple and easy to implement. The most important pretreatment methods are biological degradation, coagulation/flocculation, microfiltration (MF), and ultrafiltration (UF) (Van der Bruggen et al., 2004). MF reduces the concentration of bacteria, colloids, turbidity, and dissolved compounds associated with particles (Reiss et al., 1999). The main effect of a MF treatment is the prevention of long-term NF flux decrease which has significant implications on cost factors (Chellam et al., 1998). A similar effect is obtained with UF, which has the same operating principles as MF, but with smaller pores and a lower permeate flux per unit-membrane area. Given the large difference in water permeability between UF and MF, the latter process is usually advantageous (Van der Bruggen et al., 2004).

In addition to the effect on permeate flux, feed solution ionic concentration influences the NF rejection mechanisms, in particular the Donnan potential. The benefit of the Donnan potential in the form of increased rejection is greatest at mid salinities (1000 mg/L < TDS < 3000 mg/L). At very low salinity (TDS < 300 mg/l) the concentration of anions and cations is so low that the Donnan potential is negligible. The Donnan potential is also affected at high feed salinity. An increase in feed salinity beyond 3000 mg/L weakens the Donnan potential and leads to a decrease in membrane rejection (Batlers et al., 2005). This can be based on theory that, enhancing solution ionic concentration also increases ion concentration on membrane surface, therefore
“shielding” solutions counter-ions from membranes repulsion, as reported in Figure 2.13. Further increase in solute concentration gradually reduces Donnan potential to a point where it is no longer effective rejection mechanism, which leads to increased ion permeation (Ong et al., 2002).

![Diagram showing ion concentrations and membranes](image)

**Figure 2.13.** An increase in feed ion concentration leads to an increase in cation concentration at the membrane surface which shields the repulsive force of the membrane’s negative charge on the anions in the bulk solution (Batlers et al., 2005).

**Feed solution pH**

The membrane charge density and charge polarity are both characterized by the zeta potential (ZP) of the membrane surface, usually evaluated from streaming potential analyses. A positive or negative ZP indicates a positively or negatively charged membrane surface, respectively. Higher the ZP value, the denser is the membrane surface charge.

The main factor affecting membrane surface charge, charge density and elements rejection is the feed solution pH. In fact, it has a significant effect on ZP, because it dictates the charge on the functional groups of the membrane material and of the molecules in solution (Mullet et al., 2014). The solution pH at which the net membrane charge is zero is the iso-electric point (IEP). By reducing solution pH with acid, the amount of positively charged functional groups increases thus changing the membrane net surface charge to positive, resulting in a positive ZP. Positive surface charge reduces retention of anionic compounds (dissociated acids), while increasing retention of cationic compounds (metal ions). Positive surface charge of the membrane leads to separation process where acid fractions are typically permeated while metal ions are retained to some extent (Tanninen et al., 2002).

The pH effect on NF membrane charge and ions rejection for a mine water has been well shown by Mullet et al. (2014) in Figure 2.14. It can be noticed that cations were highly rejected (Rej>95%) when the membrane was positively charged (pH < 3), but the rejection decreased as the membrane became increasingly negative (at pH > 3). An opposite trend was observed for sulphur rejections, increasing at higher pH.
While metal removal is favored at lower pH values, fouling of membranes by substances such as organic matter or other co-ions is well known to increase with decreasing pH (Clark et al., 1993). Thus, challenges in applying NF to metal recovery may include finding a balance between removal and fouling. This can be overcome by a pH adjustment as pretreatment to nanofiltration to set the feed pH at the optimum operation condition for the target ions to be separated.

### 2.3.3. Membrane filtration cost model

Currently, one of the critical requirements in membrane technology is to achieve the optimal or most cost-effective design and operating conditions or, equivalently, to accomplish better separation performance per unit cost. Although much work has been published in the literature on the nanofiltration performance, there is relatively little literature and experience regarding the numerical design and optimization of this process from an economic standpoint (Sethi et al., 2001). It is important to use a cost model to evaluate the sensitivity of capital and operating costs to design and operating parameters in preliminary cost estimates for pressure-driven membrane-filtration facilities (Pickering et al., 1993).

The economics of membrane filtration are determined by the initial investment made towards the membrane modules along with ancillary equipment and facilities, and the various operating costs incurred over the useful life of the facility (Sethi et al., 2000). An overview of the capital and operating cost model developed by Wiesner et al. (1994) and Sethi et al. (2000a) is described in the following paragraphs.
Capital costs
Capital costs are disaggregated into non-membrane costs and the initial cost of the membrane. Non-membrane costs include all equipment and facilities necessary to support the use of membranes, such as pumps, monitoring equipment, pipes, valves, automation, tanks, frames and miscellaneous. These non-membrane costs are assumed to be correlated with the number of installed membrane modules. The number of installed modules is in turn a function of the membrane area required to produce the design flow (Pickering et al., 1993). The required membrane area, $A_{mem}$, to treat the design flow, $Q_{des}$, is calculated from the ratio of the required design capacity to the net permeate flux after backflushing, as reported by Wiesner et al. (1994) in Equation 2.5:

$$A_{mem} = \frac{Q_{des} t_{tot}}{J_{m} t_{o} - J_{bf} t_{bf}}$$  \hspace{1cm} (2.5)

where
- $J_{m}$: time-averaged permeate flux [LMH];
- $J_{bf}$: backflush flux [LMH];
- $t_{bf}$: backflush duration [h];
- $t_{o}$: operating time between two flux enhancement cycles [h];
- $t_{tot} = to + tbf$: total time for one complete operating and flux enhancement cycle [h].

The specific capital costs per cubic meter treated ($C_{cap}$) are calculated by Sethi et al. (2000) as the sum of capital costs for membrane ($C_{mem}$), pipes and valves ($C_{pv}$), instruments and controls ($C_{ic}$), tanks and frames ($C_{tf}$), miscellaneous ($C_{mi}$) and pumps ($C_{pump}$) amortized over the design life of the plant and normalized for the annual design capacity of the facility, as reported in Equation 2.6:

$$C_{cap} = \frac{(C_{mem} + C_{pv} + C_{ic} + C_{tf} + C_{mi} + C_{pump}) (\frac{A}{P})}{Q_{des}}$$  \hspace{1cm} (2.6)

The amortization factor ($\frac{A}{P}$) used to annualize the capital costs is calculated as:

$$\left(\frac{A}{P}\right) = \frac{i_{c}(1+i_{c})^{DL}}{(1+i_{c})^{DL}-1}$$  \hspace{1cm} (2.7)

where $i_{c}$ and DL are respectively the discount rate for capital investments and the design life of the plant.
The functional forms for capital cost components are reported in Table 2.3.

**Table 2.3.** Functional forms for capital cost components (Sethi et al., 2001).

<table>
<thead>
<tr>
<th>Capital cost component</th>
<th>Functional form</th>
</tr>
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<tbody>
<tr>
<td>Membranes</td>
<td>( C_{\text{mem}} = C_{\text{mem}}^* A_{\text{mem}} )</td>
</tr>
<tr>
<td>Pipes and valves</td>
<td>( C_{\text{pp}} = 5.926.13 (A_{\text{mem}})^{0.42} )</td>
</tr>
<tr>
<td>Instruments and controls</td>
<td>( C_{\text{IC}} = 1.445.50 (A_{\text{mem}})^{0.60} )</td>
</tr>
<tr>
<td>Tanks and frames</td>
<td>( C_{\text{TP}} = 3.047.21 (A_{\text{mem}})^{0.53} )</td>
</tr>
<tr>
<td>Miscellaneous equipment and facilities</td>
<td>( C_{\text{sg}} = 7.865.02 (A_{\text{mem}})^{0.57} )</td>
</tr>
<tr>
<td>Pumps</td>
<td>( C_{\text{pump}} = I \cdot f_1 \cdot f_2 \cdot L \cdot 81.27 \cdot (Q_{\text{des}} / P_{\text{f}})^{0.29} )</td>
</tr>
<tr>
<td></td>
<td>( I = 2.28 ) (this work) (^{a} )</td>
</tr>
<tr>
<td></td>
<td>( f_1 = 1.5 ) (this work) (^{b} )</td>
</tr>
<tr>
<td></td>
<td>( f_2 = 1.0 ) (for suction pressures up to 150 psi)</td>
</tr>
<tr>
<td></td>
<td>( L = 1.4 ) (this work) (^{f} )</td>
</tr>
</tbody>
</table>

**Operating costs**

Key operation and maintenance components for NF process typically include membrane replacement (\( C_{\text{mr}} \)), energy requirements (\( C_{\text{energy}} \)), chemicals (\( C_{\text{chemical}} \)) and concentrate disposal (\( C_{\text{disposal}} \)) (Pickering et al., 1993) as described in Equation 2.8:

\[
C_{\text{oper}} = C_{\text{mr}} \left( \frac{A}{f} \right) + C_{\text{energy}} + C_{\text{chemical}} + C_{\text{disposal}} \tag{2.8}
\]

The amortization factor \( \left( \frac{A}{f} \right) \) to annualize the membrane replacement costs is calculated as:

\[
\left( \frac{A}{f} \right) = \frac{if}{(1+if)^{ML}-1} \tag{2.9}
\]

where \( i_f \) and ML are respectively the discount rate for membrane replacement and the expected average membrane life.

The functional forms for operating cost components are reported in Table 2.4.
### Table 2.4. Functional forms for operating cost components (Sethi et al., 2001).

<table>
<thead>
<tr>
<th>Operating cost component</th>
<th>Functional form</th>
</tr>
</thead>
<tbody>
<tr>
<td>Membrane replacement</td>
<td>( C_{mem} = \frac{C_{\text{kin}} A_{\text{mem}}}{Q_{\text{mem}}} )</td>
</tr>
<tr>
<td>Energy</td>
<td>( C_{\text{energy}} = \frac{C_{\sigma} + C_{\gamma} + C_{\text{eff}}}{Q_{\text{mem}}} )</td>
</tr>
<tr>
<td>Energy invested in pumping feed</td>
<td>( C_{\sigma} = c_{\sigma} E_f )</td>
</tr>
<tr>
<td>Energy invested in recirculation</td>
<td>( C_{\gamma} = c_{\gamma} E_r )</td>
</tr>
<tr>
<td>Energy invested in backflushing</td>
<td>( C_{\text{eff}} = c_{\text{eff}} E_{\text{ff}} )</td>
</tr>
<tr>
<td>Energy invested in fastflushing</td>
<td>( C_{\text{eff}} = c_{\text{eff}} E_{\text{ff}} )</td>
</tr>
<tr>
<td>Chemicals</td>
<td>( C_{\text{chemical}} = \frac{Q_f CH_d CH_e}{Q_{\text{mem}}} )</td>
</tr>
<tr>
<td>Concentrate disposal</td>
<td>( C_{\text{disposal}} = \frac{(c_{\text{kw}} P_{\text{f}} Q_{\text{f}})}{Q_{\text{mem}}} + \left(CH_d CH_e Q_{\text{f}}\right) )</td>
</tr>
</tbody>
</table>

where:

- \( E_f \): rate of energy consumption of backflush (kWh);
- \( E_r \): rate of energy consumption of feed pump (kWh);
- \( E_{\text{ff}} \): rate of energy consumption of fastflush (kWh);
- \( E_{\text{rec}} \): rate of energy consumption of recycle pump (kWh);
- \( f_f \): Fanning friction factor (-);
- \( L_e \): membrane element length (m);
- \( P_{bf} \): backflush pressure (bar);
- \( P_f \): feed pressure (bar);
- \( P_r \): pressure drop across module (bar);
- \( Q_{bf} \): backflush flow rate (m³ h⁻¹);
- \( Q_{f} \): feed flow rate (m³ h⁻¹);
- \( Q_{\text{ff}} \): fastflush flow rate (m³ h⁻¹);
- \( Q_{r} \): recycle flow rate (m³ h⁻¹);
- \( Q_t \): total flow rate (m³ h⁻¹);
- \( Q_w \): waste flow rate (m³ h⁻¹);
- \( R \): recovery (Qp/Qf) (-);
- \( R \): Reynolds number (-);
- \( U_{\text{ff}} \): average fastflush velocity (m h⁻¹);
- \( U_m \): average crossflow velocity at membrane midpoint (m h⁻¹);
- \( U_{\text{in}} \): average crossflow velocity at membrane inlet (m h⁻¹);
- \( \eta_{\text{bf}} \): efficiency of backflush pump (-);
- \( \eta_{f} \): efficiency of feed pump (-);
- \( \eta_{r} \): efficiency of recycle pump (-).

Symbols:
- \( a_{\text{kin}} \): kinetic energy coefficient (-);
- \( CH_d \): coagulant cost ($ kg⁻¹);
- \( CH_e \): coagulant dose (kg m⁻³);
- \( c_{\text{kw}} \): cost of one kilowatt-hour of electricity ($ kWh⁻¹);
- \( D_e \): membrane element diameter (m);
- \( E_{\text{bf}} \): rate of energy consumption of backflush (kWh);
- \( E_{\text{ff}} \): rate of energy consumption of fastflush (kWh);
- \( f_f \): Fanning friction factor (-);
- \( L_e \): membrane element length (m);
- \( P_{bf} \): backflush pressure (bar);
- \( P_f \): feed pressure (bar);
- \( P_r \): pressure drop across module (bar);
- \( Q_{bf} \): backflush flow rate (m³ h⁻¹);
- \( Q_{f} \): feed flow rate (m³ h⁻¹);
- \( Q_{\text{ff}} \): fastflush flow rate (m³ h⁻¹);
- \( Q_r \): recycle flow rate (m³ h⁻¹);
- \( Q_t \): total flow rate (m³ h⁻¹);
- \( Q_w \): waste flow rate (m³ h⁻¹);
- \( R \): recovery (Qp/Qf) (-);
- \( R \): Reynolds number (-);
- \( U_{\text{ff}} \): average fastflush velocity (m h⁻¹);
- \( U_m \): average crossflow velocity at membrane midpoint (m h⁻¹);
- \( U_{\text{in}} \): average crossflow velocity at membrane inlet (m h⁻¹);
- \( \eta_{\text{bf}} \): efficiency of backflush pump (-);
- \( \eta_{f} \): efficiency of feed pump (-);
- \( \eta_{r} \): efficiency of recycle pump (-).
2.4. Design of Experiments (DoE)

Membrane and operating conditions selection is an important means to minimize membrane fouling, capital and operating costs. The experiments to determine the optimum conditions are conventionally conducted in such a manner as to study one factor at a time. When the experimentation object is to understand if interactions between two or more factors can affect the response, this conventional approach may result in incorrect conclusions because of ignoring interaction of factors. Statistical experimental designs, described as Design of Experiments (DoE), can be used to investigate the main effect of each factor alone on the response and the interaction effects of all the possible combinations of the factors by making fewer possible experiments (Gonder et al., 2011). Among the main benefits of the DoE methodology must be highlighted the greater estimation accuracy for each individual factor main effect on response, the minimization of number of experiments and hence decrease of costs, and a considerable reduction in the error variance, thus allowing collected data to be obtained with little influence of external factors which cannot be controlled by the experimenter. In fact, a well-planned experimental design can help to distinguish the factor effect, which the experimenters are interested in, from the experimental error.

Finally, while with the conventional method multivariate modeling is more difficult, with DoE methodology instead it is easier to get.

Several methods are available for the design of experiments to optimize the processing parameters. The choice of an experiment design plan depends on the object and the number of factors to be investigated.

When a small number of factors and levels are investigated a full factorial design, including all possible combinations of all factors at all levels, can be selected. For two factors at p levels, $2^p$ experiments are needed for a full factorial design. However, since the information achieved from the experimental results increases with the number of factors and levels and, as consequence, to the required number of trials, it is essential for the experimenters to balance the desired level of information and the amount of available resources. It is important to notice that minimizing the number of investigated levels to a two-level design, only the linear behavior can be revealed, but it cannot find quadratic effects.

In case the research goal is the process optimization, the focus will be on designs that are good for fitting quadratic models. Response Surface Methodology (RSM) is a DoE technique that is useful for optimizing processes. The most extensive applications of RSM are in the situation where several input variables potentially influence some performance measure of the process. Thus, the performance measure is called the
response, $Y$. The input variables, or factors $x_i$, are subject to the control of the scientist or engineer. Response surface methodology is a statistical modeling technique used to evaluate the relationship between the set of experimental factors ($x_i$) and observed response ($Y$). For the case of two variables, the second-order response surface relationship is described by the model reported in Equation 2.10.

$$Y = \beta_0 + \beta_1x_1 + \beta_2x_2 + \beta_11x_1^2 + \beta_22x_2^2 + \beta_12x_1x_2$$

(Malaisamy et al., 2000) summarized the four major steps involved in an optimization process as:

1) Design the experiments selecting one of the RSM designs. The most commonly used RSM design is the Central Composite Design (CCD). CCD has three different design points: edge points as in two-level designs ($\pm1$), star points at $\pm\alpha$ ($|\alpha| \geq 1$) that take care of quadratic effects and central points. Three variants exist: circumscribed (CCC), inscribed (CCI) and face centred (CCF) designs, depending on the relative location of the star and edge points, as illustrated in Figure 2.15.

![Figure 2.15](image.png)

**Figure 2.15.** Two-factor Central Composite Designs. From left to right: Circumscribed (CCC), face centred (CCF) and inscribed (CCI) designs (Chaudhary, 2014).

2) Perform the statistically designed experiments.

3) Estimate the coefficients in the response surface mathematical model and predict the response, checking the adequacy of the model.

4) Obtain the combination of factor values that optimizes the response within the region of the two-dimensional observation space.

In conclusion, a well-designed DoE is a statistical methodology that can be used as a support by the experimenter, who takes into account all possible variables and makes assumptions based on his prior complete understanding of the mechanisms behind the process.
2.5. Bibliography


74. Chaudhary S. (2014). Design of Experiments (DoE) and Development of Design Space (DS).
Chapter 3 - Materials and Methods

In the present chapter, the procedures adopted during the experimental study are described.

First of all, the preparation of synthetic leachate and NF feed solutions is explained in Chapter 3.1. The experimental tests have been organized into:

1. Pretreatment tests, including pH adjustment and filtration steps [Chapter 3.2.];
2. Tests for nanofiltration membrane characterization [Chapter 3.3.3 and 3.3.4];
3. Cross-flow nanofiltration tests, varying the operating conditions [Chapter 3.3.5 and 3.3.6];
4. Fouling analysis on the material rejected by the NF membranes [Chapter 3.3.7].

The analytical procedures and instruments used in the experiments are described in Chapter 3.4. After that, Chapter 3.5 shows the parameters and equations applied in the cost model. Finally, the software used for data analysis are listed in Chapter 3.6.

3.1. Solutions preparation

The synthetic leachate and the NF feed solutions used in the pretreatment and nanofiltration tests have been prepared according to the procedure described below.

Solutions’ preparation was carried out using purified nanopure (NP) water and includes different steps:

- Addition of salts and REEs solutions in 1 L of NP water, hand mixing after each addition to make sure all the salts are dissolved. Chemicals are presented in Table 3.1 and 3.2 with their amounts.

<table>
<thead>
<tr>
<th>IUPAC Name</th>
<th>Formula</th>
<th>Synthetic Leachate (g per 1L)</th>
<th>NF Feed (g per 1L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium nitrate</td>
<td>NaNO3</td>
<td>39.156</td>
<td>43.212</td>
</tr>
<tr>
<td>Magnesium nitrate hexahydrate</td>
<td>Mg(NO3)2·6H2O</td>
<td>0.216</td>
<td>0.222</td>
</tr>
<tr>
<td>Calcium nitrate tetrahydrate</td>
<td>Ca(NO3)2·4H2O</td>
<td>0.484</td>
<td>0.523</td>
</tr>
<tr>
<td>Aluminum nitrate nonahydrate</td>
<td>Al(NO3)3·9H2O</td>
<td>7.53</td>
<td>3.823</td>
</tr>
<tr>
<td>Iron(III) nitrate nonahydrate</td>
<td>Fe(NO3)3·9H2O</td>
<td>1.298</td>
<td>0.029</td>
</tr>
</tbody>
</table>
Table 3.2. REEs used for synthetic leachate and NF feed preparation.

<table>
<thead>
<tr>
<th>IUPAC Name</th>
<th>Formula</th>
<th>Synthetic leachate (µL per 1L)</th>
<th>NF Feed (µL per 1L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Terbium</td>
<td>Tb</td>
<td>300</td>
<td>280</td>
</tr>
<tr>
<td>Neodymium</td>
<td>Nd</td>
<td>300</td>
<td>280</td>
</tr>
<tr>
<td>Yttrium</td>
<td>Y</td>
<td>300</td>
<td>280</td>
</tr>
<tr>
<td>Europium</td>
<td>Eu</td>
<td>300</td>
<td>280</td>
</tr>
<tr>
<td>Erbium</td>
<td>Er</td>
<td>300</td>
<td>280</td>
</tr>
<tr>
<td>Dysprosium</td>
<td>Dy</td>
<td>300</td>
<td>280</td>
</tr>
</tbody>
</table>

- Addition of 20 mL of nitric acid, HNO₃, hand mixing to make sure the nitric acid is homogeneously distributed in the solution volume.
- Addition of 12.006 g and 5.285 g of sodium metasilicate nonahydrate, Na₂Si(NO₃)₃·9H₂O, to the solutions for the synthetic leachate and NF feed preparation, respectively.
- After hand shaking to dissolve also the last salt added, the solution flask is filled up with NP water until a final volume of 2 L. The final solution is mixed by hand shaking.
- The pH of the prepared solutions is 0.95 and 0.82 for synthetic leachate and NF feed, respectively. The NF feed preparation proceeds with the addition of 55 mL of 5N NaOH to increase the pH at a final value of 3.5.
- Nanofiltration experiments were carried out with NF feed at three different pH values: 1.5, 2.5 and 3.5. The last step for NF feed preparation is the addition of 2.6 and 0.36 mL of 15.7 M HNO₃ to adjust the pH to 1.5 and 2.5, respectively.
- Solution conductivity has been measured.

The 5N NaOH solution used for pH adjustments has been prepared dissolving 20 g of NaOH (Sigma-Aldrich 71687) in 80 mL of NP water in a beaker mixed with a magnetic stirrer. Once cooled, the final volume was brought to 100 mL.

3.2. Pretreatment tests

3.2.1. Coarse pre-filtration

A coarse pre-filtration step has been performed on 4 L real leachate, to remove the solids remaining after the acid leaching process. The real leachate has been filtrated through filters with a glass filter funnel, shown in Figure 3.1. The filtration was carried out with 47 mm diameter, 1µm pore size, polycarbonate (PC) filters (Table 3.9).
3.2.2. pH adjustment test
Two repetitions of pH adjustment tests have been carried out on fourteen 150 mL synthetic leachate samples. One sample was kept at the initial pH of 0.95. The other 13 samples have been kept mixed on a magnetic stirrer with a pH probe submerged to measure the solution pH over time during the base dosage. A 5N NaOH solution was dosed to the samples to increase the pH from 0.95 to different final pH values: 1.5, 2, 2.25, 2.5, 2.75, 3, 3.25, 3.5, 3.75, 4, 4.25, 4.5, 5. After the base dosage, the magnetic stirrer was stopped and a sample was taken from the supernatant. The concentrations of REEs and major elements in the supernatant have been measured (Chapter 3.4). The system, including the magnetic stirrer and the pH probe, is presented in Figure 3.2.

Figure 3.1. Glass filter funnel used for the real leachate coarse pre-filtration (a), solids collected on the filter (b).

Figure 3.2. System used for pH adjustment tests: magnetic stirrer, pH probe, pH meter.
3.2.3. Pre-filtration test

Pre-filtration tests have been performed on synthetic and real leachate samples after pH adjustment. For the first step of the pre-filtration test, a volume of 5 mL of the samples have been filtrated through the filtration system explained in paragraph 3.2.1 with the addition of a falcon tube used to collect the filtrate, as shown in Figure 3.3. After filtration, solid content filtered were evaluated and the filtrated solution was analyzed for its REEs and major elements concentrations.

![Glass filter funnel with addition of falcon tube used for pre-filtration tests.](image)

The pre-filtration tests have been carried out varying pH, filters materials, filters pore sizes and precipitation times between pH adjustment and pre-filtration, as summarized in Table 3.3, where the number of experiments performed for each combination is also reported.
Table 3.3. Operating parameters in pre-filtration tests.

PES: Polyethersulfone; MCE: Mixed Cellulose Ester; PC: Polycarbonate.

<table>
<thead>
<tr>
<th>Feed solution</th>
<th>pH (/)</th>
<th>Filter pore size (μm)</th>
<th>Filter Material</th>
<th>Precipitation time (min)</th>
<th>Tests number</th>
</tr>
</thead>
<tbody>
<tr>
<td>Synthetic Leachate</td>
<td>3.25</td>
<td>0.22 PES</td>
<td>0</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.45 MCE</td>
<td>0, 20, 40, 60, 90</td>
<td>2 per precipitation time</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3.5</td>
<td>0.22 PES</td>
<td>0</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.45 MCE</td>
<td>0, 20, 40, 60, 90</td>
<td>2 per precipitation time</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3.75</td>
<td>0.22 PES</td>
<td>0</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.45 MCE</td>
<td>0, 20, 40, 60, 90</td>
<td>2 per precipitation time</td>
<td></td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>0.22 PES</td>
<td>0</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.45 MCE</td>
<td>0, 20, 40, 60, 90</td>
<td>2 per precipitation time</td>
<td></td>
</tr>
<tr>
<td></td>
<td>4.25</td>
<td>0.22 PES</td>
<td>0</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.45 MCE</td>
<td>0, 20, 40, 60, 90</td>
<td>2 per precipitation time</td>
<td></td>
</tr>
<tr>
<td>Real Leachate</td>
<td>4</td>
<td>0.45 MCE</td>
<td>0</td>
<td>1</td>
<td></td>
</tr>
</tbody>
</table>

Filter pore size effect has been analyzed looking at the weight of the chemical precipitates rejected by each filter.
The feed pH and precipitation time effects on the pre-treatment performance has been studied analyzing the major elements and REEs concentrations in the pre-filtration permeate flow.

3.3. Nanofiltration tests

3.3.1. Membranes

Four commercial polymeric NF membranes were employed in this study: NP010 (MicroDyn-Nadir), NP030 (MicroDyn-Nadir), DK (GE Osmonics), Duracid (GE Osmonics). The membrane specifications provided by the manufacturers are shown in Table 3.4.
Table 3.4. Membrane specifications given by the manufacturers.

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>NP010</th>
<th>NP030</th>
<th>DK</th>
<th>Duracid</th>
</tr>
</thead>
<tbody>
<tr>
<td>Manufacturer</td>
<td>Microdyn-Nadir</td>
<td>GE W&amp;P Technologies</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Website</td>
<td><a href="http://www.microdyn-nadir.com">www.microdyn-nadir.com</a></td>
<td><a href="http://www.geawater.com">www.geawater.com</a></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Classification</td>
<td>NF</td>
<td>NF</td>
<td>NF</td>
<td>NF</td>
</tr>
<tr>
<td>Polymer</td>
<td>Permanently hydrophilic PES</td>
<td>Thin Film (1)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pmax [bar]</td>
<td>40</td>
<td>40</td>
<td>40</td>
<td>60</td>
</tr>
<tr>
<td>Tmax [°C]</td>
<td>95</td>
<td>95</td>
<td>50</td>
<td>70</td>
</tr>
<tr>
<td>pH</td>
<td>0-14</td>
<td>0-14</td>
<td>1-10</td>
<td>0-9</td>
</tr>
<tr>
<td>MWCO [Dalton]</td>
<td>~ 1000</td>
<td>~ 500</td>
<td>~ 150-300</td>
<td>~ 150-200</td>
</tr>
<tr>
<td>Pure water flux</td>
<td>5-10</td>
<td>1-1.8</td>
<td>5.5 ± 25%</td>
<td>1.1 - 2.1</td>
</tr>
<tr>
<td>[L/h/m²/bar]</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Salt rejection [%]</td>
<td>35-75 (2)</td>
<td>80-95 (2)</td>
<td>96 (3)</td>
<td>98 (3)</td>
</tr>
</tbody>
</table>

(1) poly (piperazine-amide) based interfacial polymerization membrane on a polysulfone support layer and two proprietary layers backed by a polyester support (Vandezande, 2008)

(2) Tested salt: Na₂SO₄

(3) Tested salt: MgSO₄

3.3.2. Cross-flow filtration system

Pure water permeability and nanofiltration tests were conducted using a cross-flow flat sheet membrane filtration system. The cross-flow SEPA CF II cell (GE Osmonics, Minnetonka, MN, USA), shown in Figure 3.4, has been used for this purpose. A stainless steel cell unit is composed by a bottom cell body, a top cell body and a pair of laterally spaced viton O-rings forming a seal in between. The bottom cell body is provided with a feed and concentrate spacer cavity and the top cell body is provided with a permeate carrier cavity. The membrane is inserted in the cell with its active layer facing down. The active membrane area, that is the one inside the inner O-ring, is equal to 135 cm². The cell body is closed and inserted in a stainless steel cell holder, with pressure gauge and piston. The cell holder is pressurized by a hydraulic hand pump with a pressure of 40 bar, bigger than the transmembrane pressure applied during the experiments, to avoid the opening of the cell body and solution leakage.
Figure 3.4. Cell body internal configuration without (a) and with (b) the membrane. Cell system including cell body and cell holder (c).

The system includes a feed tank, containing the feed that is sent to the membrane cell by a high-pressure pump. Feed, concentrate and permeate line are made by stainless steel. On the feed and concentrate lines there are the feed and back pressure valve used to control feed flow rate, transmembrane pressure and permeate recovery. The scheme, shown in Figure 3.5, is completed with the measurement system composed by two batches placed on two balances, connected to the computer, used to measure the permeate and concentrate fluxes and collect their samples.
3.3.3. **Membrane water permeability test**

Pure water permeability measurements were conducted with NP water on the four tested membranes.

As in all the NF tests performed in this study, at first, membrane was filtered with NP water without circulating retentate and permeate back to the feed tank so that the impurities were washed out from the system. Afterwards, the system was put in the circulation mode and the membrane was compacted for 2 hours at a constant pressure of 25 bar to obtain stable membrane structure. Permeability was evaluated at three different increasing pressures (12, 18, 24 bar) for each membrane. Permeate flux was measured manually by weighing method. After setting the pressure to the aimed value, the flux was stabilized in 10-20 minutes before conducting the measurement. Mass of permeate was collected in a batch placed on the balance and weighted every 5 seconds.

---

**Figure 3.5.** Nanofiltration cross-flow system schematics (a) and real system (b).
for 3 minutes, three times during 30-minute measurement period. The average gave the flux of the first measurement. Afterwards, pressure was increased to conduct the next flux measurement. Figure 3.6 presents the permeate mass data collection set up.

![Permeate mass data collection set up.](image)

**Figure 3.6.** Permeate mass data collection set up.

The measured permeate masses were used to calculate permeate fluxes which were plotted as a function of pressure to obtain membrane pure water permeability. Calculation of permeate flow results from mass collection data over time, according to Equation 3.1.

\[
Q_p = \frac{m_p}{t_c \rho}
\]

**Equation 3.1**

where:
- \(Q_p\): permeate flow through membrane \([\text{l/h}]\)
- \(m_p\): mass of collected permeate \([\text{kg}]\)
- \(t_c\): collection time \([\text{h}]\)
- \(\rho\): NP water density \([\text{kg/l}]\)

Obtained permeate flows for each membrane at different pressures were then used to calculate flux as presented in Equation 3.2.

\[
J = \frac{Q_p}{A_m}
\]

**Equation 3.2**

where:
- \(J\): membrane flux \([\text{LMH}]\)
- \(A_m\): membrane surface area \([\text{m}^2]\)
The calculated fluxes for each membrane were then used to calculate membrane specific pure water permeability, or membrane constant, determined from the slopes of the flux curves plotted as a function of the transmembrane pressure differences, as in Equation 3.3.

\[
L_p = \frac{\Delta J}{\Delta p}
\]

where:
- \(L_p\): membrane pure water permeability [LMH/bar]
- \(\Delta J\): membrane flux difference [LMH]
- \(\Delta p\): pressure difference [bar]

### 3.3.4. Surface Zeta potential

The NP010, NP030, DK and Duracid membranes zeta potentials have been determined through the tangential streaming potential (TSP) method, that consists in the measurement of the electric potential increase when an electrolyte solution passes between two membrane samples facing their active layers under different applied pressure gradients. These measurements were performed using an electrokinetic analyzer ZetaCAD. For each experiment 2 bare membrane samples of 20 mm × 10 mm were used and streaming current was measured in a 0.1 M KCl solution at 25 °C. The pH of the electrolyte solution was adjusted between 2.9 and 11.5 through addition of a 0.1 M HNO3 or NaOH solution. The zeta potential is calculated according to Equation 3.4.

\[
\zeta = \frac{\nu_p \lambda_0 \eta}{\varepsilon_0 \varepsilon_b} \tag{3.4}
\]

where:
- \(\zeta\): zeta potential [V]
- \(\nu_p = dE/dP\): streaming potential [V/Pa]
- \(\lambda_0\): solution average conductivity [S/cm]
- \(\eta\): electrolyte dynamic viscosity [Pa s]
- \(\varepsilon_0\): vacuum permittivity
- \(\varepsilon\): dielectric constant of the electrolyte
3.3.5. Experimental plan for cross flow nanofiltration tests

Nanofiltration experiments have been performed on pre-treated synthetic and real leachates, called Synthetic NF Feed and Real NF Feed, respectively. The experiments have been carried out in the cross-flow system described in Chapter 3.3.2.

Design of Experiments methodology was applied to support the nanofiltration experimental plan decisions. A two-level full factorial design and a central composite face-centered (CCF) design were identified as the most effective for the purpose of the process optimization study.

Firstly, a two-level full factorial design was prepared, as reported in Table 3.5 and Figure 3.7. According to the developed design, 4 experiments were performed filtering the synthetic leachate at different pH and pressures using four membranes (NP010, NP030, DK, Duracid), with a total of 16 experiments carried out.

### Table 3.5. Experimental plan (full factorial design) with factors and levels considered in each experiment.

<table>
<thead>
<tr>
<th>Factor</th>
<th>-</th>
<th>+</th>
</tr>
</thead>
<tbody>
<tr>
<td>A: pH</td>
<td>1.5</td>
<td>3.5</td>
</tr>
<tr>
<td>B: Pressure [bar]</td>
<td>12</td>
<td>24</td>
</tr>
</tbody>
</table>

### Figure 3.7. 2-level full factorial design (left) and central composite face-centered design (right) for pressure and pH factors.

In addition, at a second stage, a central composite face-centered (CCF) design was performed adding the star and central points at the center of each face of the factorial design.
space. Thus, the distance between star and central points is \( \alpha = \pm 1 \) and three levels were used, as shown in Table 3.6 and Figure 3.7. According to the developed design, sets of 9 experiments were performed with DK membrane on the synthetic leachate in two repetitions, and ten central point’s replicates. A total of 26 experiments have been carried out.

Table 3.6. Experimental plan (CCF design) with factors and levels considered in each experiment.

<table>
<thead>
<tr>
<th>Factor</th>
<th>-</th>
<th>0</th>
<th>+</th>
</tr>
</thead>
<tbody>
<tr>
<td>A: pH</td>
<td>1.5</td>
<td>2.5</td>
<td>3.5</td>
</tr>
<tr>
<td>B: Pressure [bar]</td>
<td>12</td>
<td>18</td>
<td>24</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>#</th>
<th>A</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>-</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>-</td>
<td>+</td>
</tr>
<tr>
<td>4</td>
<td>0</td>
<td>-</td>
</tr>
<tr>
<td>5</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>6</td>
<td>0</td>
<td>+</td>
</tr>
<tr>
<td>7</td>
<td>+</td>
<td>-</td>
</tr>
<tr>
<td>8</td>
<td>+</td>
<td>0</td>
</tr>
<tr>
<td>9</td>
<td>+</td>
<td>+</td>
</tr>
</tbody>
</table>

After the conclusion of these two sets of experiments, an additional experiment has been performed on real NF feed with DK membrane at feed pH and applied pressure equal to 3.5 and 12 bar, respectively.

3.3.6. Experimental procedure for cross flow nanofiltration tests

Each cross flow nanofiltration experiment has been performed with the procedure explained below.

After compaction, described in paragraph 3.3.3, the system volume has been completely emptied and the feed tank has been filled with the experiment feed solution. The feed pump was set to send a feed flow rate equal to \( Q_F = 0.384 \) L/h to the membrane. Both permeate and concentrate have been recirculated in the feed tank, not to vary the feed solution composition. The selected pressure for the experiment was set closing or opening the back pressure valve on the concentrate line. After setting the pressure to the selected value, the flux was stabilized in around 1 hour before conducting the measurements.

Concentrate and permeate flow rates have been measured as explained in Chapter 3.3.3.

After flux measurement, 3 mL concentrate and permeate samples have been collected and their REEs and major elements concentrations have been measured.
At the end of the experiment, the system was emptied, the membrane was removed and collected for further studies, explained in chapter 3.3.7. Finally, 4 L of NP water were circulated in the system to clean it.

Permeate flux, resulting from permeate mass collection data over time, has been calculated with the same procedure explained in chapter 3.3.3.

Permeate recovery has been calculated from the concentrate and permeate flow rates as the percentage of the feed flow passing through the membrane as permeate, as reported in Equation 3.5:

\[
\text{Rec} = \frac{Q_p}{Q_F} \cdot 100 = \frac{Q_p}{Q_p + Q_c} \cdot 100
\]  \hspace{1cm} (3.5)

where:
- \(\text{Rec}\): permeate recovery  \([\%]\)
- \(Q_p\): permeate flow rate  \([\text{l/h}]\)
- \(Q_F\): feed flow rate  \([\text{l/h}]\)
- \(Q_c\): concentrate flow rate  \([\text{l/h}]\)

The measured feed and permeate concentrations of each element, \(i\), have been used to calculate the element rejection performed by the membrane, with Equation 3.6:

\[
\text{Rej}_{i} = (1 - \frac{C_{P,i}}{C_{F,i}}) \cdot 100
\]  \hspace{1cm} (3.6)

where:
- \(\text{Rej}_{i}\): element \(i\) rejection  \([\%]\)
- \(C_{P,i}\): element \(i\) concentration in the permeate  \([\text{ppm}]\)
- \(C_{F,i}\): element \(i\) concentration in the feed  \([\text{ppm}]\)

### 3.3.7. NF Fouling Analysis

The nanofiltration fouling effect has been described with three analyses, performed on DK membranes after the NF tests, to identify the amount and chemical characteristics of the rejected elements collected on the membrane feed side surface during the cross-flow experiments.
The amount of rejected elements has been measured taking three 1 cm² membrane samples at a distance of 2 cm from the feed inlet, according to the scheme shown in Figure 3.8. The rejected particles amount has been calculated as the average difference between the weights of used membrane samples and 1 cm² bare membrane.

![Figure 3.8. Fouling amount measurement schematic. Flow direction illustrated with the black dashed arrow.](image)

### 3.4. Analytical procedure and instruments

This chapter illustrates the chemicals, filters, instruments and analytical procedures used in the pre-treatment and NF tests.

Synthetic leachate and NF feed solutions’ preparation was carried out using purified nanopure (NP) water from Elga’s CENTRA-R 60/120 equipment, which produces nanopure (NP) water with resistance of 15MΩ.

Salts, REEs solutions, acid and base chemicals used for solutions’ preparation with their producing companies and catalogue numbers are reported in Table 3.7.
Table 3.7. Salts, REEs solutions, acid and base chemicals used for solutions’ preparation with their producing companies and catalogue numbers.

<table>
<thead>
<tr>
<th>IUPAC Name</th>
<th>Formula</th>
<th>Producing company</th>
<th>Catalogue Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium nitrate</td>
<td>NaNO₃</td>
<td>Sigma-Aldrich</td>
<td>7631-99-4</td>
</tr>
<tr>
<td>Magnesium nitrate hexahydrate</td>
<td>Mg(NO₃)₂ · 6H₂O</td>
<td></td>
<td>13446-18-9</td>
</tr>
<tr>
<td>Calcium nitrate tetrahydrate</td>
<td>Ca(NO₃)₂ · 4H₂O</td>
<td></td>
<td>13477-34-4</td>
</tr>
<tr>
<td>Aluminum nitrate nonahydrate</td>
<td>Al(NO₃)₃ · 9H₂O</td>
<td></td>
<td>7784-27-2</td>
</tr>
<tr>
<td>Sodium metasilicate nonahydrate</td>
<td>Na₂Si(NO₃)₃ · 9H₂O</td>
<td></td>
<td>13517-24-3</td>
</tr>
<tr>
<td>Iron(III) nitrate nonahydrate</td>
<td>Fe(NO₃)₃ · 9H₂O</td>
<td></td>
<td>7782-61-8</td>
</tr>
<tr>
<td>Terbium</td>
<td>Tb</td>
<td>Inorganic Ventures</td>
<td></td>
</tr>
<tr>
<td>Neodymium</td>
<td>Nd</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Yttrium</td>
<td>Y</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Europium</td>
<td>Eu</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Erbium</td>
<td>Er</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dysprosium</td>
<td>Dy</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nitric acid</td>
<td>HNO₃</td>
<td>Sigma-Aldrich</td>
<td>225711-475ML</td>
</tr>
<tr>
<td>Sodium Hydroxide</td>
<td>NaOH</td>
<td>Sigma-Aldrich</td>
<td>71687</td>
</tr>
</tbody>
</table>

The pH and conductivity measurements during the solutions’ preparation and pH adjustment step have been performed submerging probes, whose characteristics are reported in Table 3.8, in the bottles containing the solutions.

Table 3.8. Characteristics of the analytical instruments used for solutions’ preparation and pH adjustment step.

<table>
<thead>
<tr>
<th>Measured Parameter</th>
<th>Instrument probe</th>
<th>Range</th>
<th>Resolution</th>
<th>Accuracy</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>Accumet, 13-620-183A</td>
<td>[-2 ; 20 ] (-)</td>
<td>0.001</td>
<td>± 0.002</td>
</tr>
<tr>
<td>Conductivity</td>
<td>Accumet, 13-620-100</td>
<td>[0 ; 500] (mS/cm)</td>
<td>0.001</td>
<td>± 1%</td>
</tr>
</tbody>
</table>

The pre-filtration tests have been performed using a glass filter funnel (VWR, 28144-624) with four different filters, whose characteristics are reported in Table 3.9.

Table 3.9. Characteristics of the filters used for the real leachate solid pre-filtration and the precipitates pre-filtration tests.

<table>
<thead>
<tr>
<th>Company</th>
<th>Catalogue number</th>
<th>Material</th>
<th>Pore size (µm)</th>
<th>Filter diameter (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Merck, MF Millipore</td>
<td>GPWP04700</td>
<td>PES</td>
<td>0.22</td>
<td>47</td>
</tr>
<tr>
<td>Merck, MF Millipore</td>
<td>HAWP04700</td>
<td>MCE</td>
<td>0.45</td>
<td>47</td>
</tr>
<tr>
<td>Merck, MF Millipore</td>
<td>AAWP04700</td>
<td>PES</td>
<td>0.8</td>
<td>47</td>
</tr>
<tr>
<td>Whatman Nuclepore</td>
<td>WHA111110</td>
<td>PC</td>
<td>1</td>
<td>47</td>
</tr>
</tbody>
</table>
The pre-filtration tests procedure is described below. For the first step of the pre-filtration test, the filters have been heated in the oven at a temperature of 105 °C for one hour to evaporate the filters’ humidity. Before the filtration, the dry filters were weighted. A volume of 5 mL of the samples have been filtrated through the filtration system explained in Chapter 3.2.1 with the addition of a falcon tube used to collect the filtrate, as shown in Figure 2.3. After filtration, the filters have been heated for one hour in the oven at 105°C to evaporate the filters' humidity. The dry filters and the separated precipitates, with a dimension bigger than the pore size of the filter, have been weighted. Then, the precipitates weight has been calculated as the difference between the dried filters weight measured after and before the filtration as:

\[ W_p = W_{f,a} - W_{f,b} \]  (3.7)

where:
- \( W_p \): rejected precipitates weight [mg]
- \( W_{f,a} \): dried filter weight after filtration [mg]
- \( W_{f,b} \): dried filter weight before filtration [mg]

The filtrated volume has been kept and its major elements and REEs concentrations have been measured.

Major elements and REEs concentrations in initial leachate, pH adjusted sample supernatants, pre-filtrated samples, NF feed, concentrate and permeate for both synthetic and real leachates have been measured by inductively coupled plasma mass spectrometry, ICP-MS (Agilent 7900 ICP-MS), shown in Figure 3.9.

![Figure 3.9. Instrument set up for ICP-MS analysis.](image)
The NF membranes zeta potential was determined by the technique of streaming potential measurement using an electrokinetic analyzer, SurPASS (Anton Paar, Austria). The instrument set up for zeta potential analysis is shown in Figure 3.10.

![Figure 3.10. Instrument set up of ZetaCAD for zeta potential analysis.](image)

DK membrane morphology and qualitative analysis of elemental composition of the rejected matrix on the membrane feed side surface were characterized respectively by emission scanning electron microscope, SEM (Philips FEI XL30) and energy dispersive X-ray spectroscopy, EDS (Bruker XFlash 4010), before and after the synthetic and real NF feed nanofiltration. The instrument set up for SEM with EDS analysis is shown in Figure 3.11.

![Figure 3.11. Instrument set up for SEM with EDS analysis.](image)
The elemental composition including chemical and oxidation state of the elements rejected by the DK membrane have been measured by X-ray photoelectron spectroscopy, XPS (Kratos Analytical Axis Ultra). The instrument set up for XPS analysis is shown in Figure 3.12.

Figure 3.12. Instrument set up for XPS analysis.

3.5. Economic model

The cost model developed in previous studies (Sethi et al., 2001) has been applied and integrated to estimate capital and operating costs for real scale nanofiltration system process. This chapter gives an overview about assumptions, schematics, cost model equations and their integration, parameters used to estimate the feasibility of the process.

3.5.1. Economic model main structure

The cost model schematic is based on the following main assumptions:

- experimented pre-treatment steps, regarding pH adjustments and pre-filtration, have been included in the model;
- spiral wound (SW) configuration has been selected as the most reliable for real scale nanofiltration process;
- SWNF concentrate, including REEs and co-metals, needs post-treatments to selectively separate REEs. Electrochemical deposition (ECD) has been assumed as post-treatment and its costs have been modeled.

The general schematic, following the above assumptions, is presented in Figure 3.13.
3.5.2. pH adjustments cost model

The pH adjustment steps have been modeled with the following assumptions:

- in-line pH adjustment with no need for precipitation tank;
- operating costs due to base and acid dosage, estimated based on laboratory experiments.

The pH adjustment steps parameters used in the economic model are reported in Table 3.10.

Table 3.10. pH adjustment steps cost model parameters.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit of measure</th>
<th>pH adjustment 1</th>
<th>pH adjustment 2</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial pH</td>
<td>/</td>
<td>0.95</td>
<td>3.5</td>
<td></td>
</tr>
<tr>
<td>Final pH</td>
<td>/</td>
<td>4</td>
<td>[1.5, 2.5, 3.5]</td>
<td></td>
</tr>
<tr>
<td>Chemical</td>
<td></td>
<td>NaOH</td>
<td>HNO3</td>
<td></td>
</tr>
<tr>
<td>Chemical dose</td>
<td>mL/L</td>
<td>26.25</td>
<td>f (Final pH)</td>
<td>Experiments</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>[1.3, 0.18, 0]</td>
<td></td>
</tr>
<tr>
<td>Title</td>
<td>mol/L</td>
<td>5</td>
<td>15.7</td>
<td>Product</td>
</tr>
<tr>
<td>Chemical density</td>
<td>g/L</td>
<td>200</td>
<td>1.413</td>
<td>Product</td>
</tr>
<tr>
<td>Chemical cost</td>
<td>$/Kg</td>
<td>0.22051</td>
<td>0.18</td>
<td>Alibaba</td>
</tr>
</tbody>
</table>

3.5.3. Membranes filtrations cost models

This chapter reports the assumptions and schematics of both the pre-filtration and nanofiltration steps. Afterwards, the actualization of the capital costs equations is explained. Finally, the parameters used in the models are summarized.
The pre-filtration step cost model has been developed with the following assumptions:
- microfiltration (MF) membrane has been considered as pre-filtration step,
- capital and operating costs from previous studies (Sethi et al., 2001) have been considered;
- capital costs have been actualized, to take in consideration the equipment cost increase from 2001 to 2015, with the equation 3.12;
- MF real scale configuration includes: concentrate recirculation, fast-flush and back-flush, concentrate disposal.

The above reported assumptions are summarized in the schematic of Figure 3.14.

![Figure 3.14. Pre-filtration configuration schematic implemented in the cost model.](image)

The nanofiltration step cost model has been developed with the following assumptions:
- capital and operating costs reported in previous studies (Sethi et al., 2001) have been considered;
- Capital costs have been actualized, to take in consideration the equipment cost increase from 2001 to 2015, with the equation 3.9;
- SWNF real scale configuration does not include: concentrate recirculation, fast-flush and back-flush;
- The permeate stream is sent to disposal.

The above reported assumptions are summarized in the schematic of Figure 3.15.
Figure 3.15. Nanofiltration configuration schematic considered in the cost model.

Capital costs for each filtration system equipment have been estimated as function of the membrane area, $A_{\text{memb}}$, in 2001 (Sethi, 2001), with the generic Equation 3.8:

$$\text{Cost}_{i(2001)} = k_i (A_{\text{memb}})^{n_i}$$  \hspace{1cm} (3.8)

To take into consideration the equipment cost increase from 2001 to 2015, capital costs have been actualized using the Chemical Engineering Plant Cost Index (CEPCI). CEPCI is a specific cost escalation factor based on statistical market data estimated for the transfer of equipment cost in time (Vatavuk, 2002). The CEPCI base, with a value of 100, considers the average equipment cost in the time interval of 1957-59. The cost actualization has been performed with Equation 3.9:

$$\text{Cost}_{i(2015)} = \frac{\text{CEPCI}_{i(2015)}}{\text{CEPCI}_{i(2001)}} \times \text{Cost}_{i(2001)} = \frac{\text{CEPCI}_{i(2015)}}{\text{CEPCI}_{i(2001)}} k_i (A_{\text{memb}})^{n_i}$$  \hspace{1cm} (3.9)

The filtration system equipments CEPCI values for 2001 (Vatavuk, 2002) and 2015 (www.chemengonline.com) are reported in Table 3.11.

<table>
<thead>
<tr>
<th>Equipment</th>
<th>CEPCI 2001</th>
<th>CEPCI 2015</th>
<th>Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pipes and valves</td>
<td>551.6</td>
<td>845.6</td>
<td>1.53</td>
</tr>
<tr>
<td>Instrument and control</td>
<td>364.5</td>
<td>402</td>
<td>1.1</td>
</tr>
<tr>
<td>Tanks and frames</td>
<td>360.3</td>
<td>609.7</td>
<td>1.69</td>
</tr>
<tr>
<td>Miscellaneous equipment</td>
<td>413.4</td>
<td>741.7</td>
<td>1.79</td>
</tr>
<tr>
<td>Pumps</td>
<td>673.3</td>
<td>958.4</td>
<td>1.42</td>
</tr>
</tbody>
</table>

The list of the parameters used in the membrane filtration systems cost models are reported in Table 3.12 with their symbols, values and sources.
The Recovery of Rare Earth Elements from coal fly ash by nanofiltration
MSc Thesis in Environmental and Land Planning Engineering- Beatrice Cantoni
Politecnico di Milano – A.Y. 2016/2017

Table 3.12. MF and SWNF cost model parameters.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>MF</th>
<th>SWNF</th>
<th>Unit</th>
<th>Source **</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plant Design life</td>
<td>20</td>
<td>20</td>
<td>years</td>
<td>[2] [4]</td>
</tr>
<tr>
<td>Ash flow rate entering</td>
<td>1000</td>
<td>kg/h</td>
<td>Real project</td>
<td></td>
</tr>
<tr>
<td>Design flow rate</td>
<td>3.435</td>
<td>3.353</td>
<td>m³/h</td>
<td>Real project</td>
</tr>
<tr>
<td>Permeate Flux</td>
<td>800</td>
<td>f (pH, Pressure)*</td>
<td>l/m²/h</td>
<td>[5] [7]</td>
</tr>
<tr>
<td>Membrane cost</td>
<td>16.1</td>
<td>26.77</td>
<td>$/m²</td>
<td>[Alibaba]</td>
</tr>
<tr>
<td>Crossflow velocity</td>
<td>1.7</td>
<td>0.15</td>
<td>m/s</td>
<td>[4] [5] [7]</td>
</tr>
<tr>
<td>Backflush pressure</td>
<td>600</td>
<td>NA</td>
<td>kPa</td>
<td>[6] [7]</td>
</tr>
<tr>
<td>Fastflush pressure</td>
<td>2.1</td>
<td>NA</td>
<td>m/s</td>
<td>[4] [5] [6]</td>
</tr>
<tr>
<td>Cleaning chemical cost</td>
<td>0.07</td>
<td>0.0013</td>
<td>$/(m³·cleaning)</td>
<td>[6]</td>
</tr>
<tr>
<td>Chemical cleaning frequency</td>
<td>21</td>
<td>30</td>
<td>days</td>
<td>[6]</td>
</tr>
<tr>
<td>Membrane life</td>
<td>5</td>
<td>5</td>
<td>years</td>
<td>[4] [5] [6]</td>
</tr>
<tr>
<td>Pumps efficiency</td>
<td>80</td>
<td>80</td>
<td>%</td>
<td></td>
</tr>
<tr>
<td>Energy cost</td>
<td>0.1</td>
<td>0.1</td>
<td>$/kWh</td>
<td></td>
</tr>
<tr>
<td>Discount rate: capital investment</td>
<td>10</td>
<td>10</td>
<td>%</td>
<td>[2]</td>
</tr>
<tr>
<td>Discount rate: membrane replace</td>
<td>8</td>
<td>8</td>
<td>%</td>
<td></td>
</tr>
<tr>
<td>Depreciation</td>
<td>0.1</td>
<td>0.1</td>
<td>year-1</td>
<td></td>
</tr>
</tbody>
</table>

* Experiments based models
** See Bibliography (Chapter 3.7)

The REEs concentrations in the membrane systems feed streams is reported in Table 3.13, with the membranes REEs rejection operated by the membranes.

Table 3.13. REEs concentrations in membranes feeds and their rejections.

<table>
<thead>
<tr>
<th>REE</th>
<th>MF Feed Concentration (g/m³)</th>
<th>MF Rejection (%)</th>
<th>MF Rejection (g/m³)</th>
<th>NF Rejection (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y</td>
<td>33.5</td>
<td>12</td>
<td>29.48</td>
<td>f (pH, Pressure)</td>
</tr>
<tr>
<td>Nd</td>
<td>26.75</td>
<td>12</td>
<td>23.54</td>
<td>f (pH, Pressure)</td>
</tr>
<tr>
<td>Eu</td>
<td>1.14</td>
<td>12</td>
<td>1.00</td>
<td>f (pH, Pressure)</td>
</tr>
<tr>
<td>Tb</td>
<td>0.9</td>
<td>12</td>
<td>0.79</td>
<td>f (pH, Pressure)</td>
</tr>
<tr>
<td>Dy</td>
<td>5.21</td>
<td>12</td>
<td>4.58</td>
<td>f (pH, Pressure)</td>
</tr>
<tr>
<td>Er</td>
<td>2.99</td>
<td>12</td>
<td>2.63</td>
<td>f (pH, Pressure)</td>
</tr>
<tr>
<td>Sc*</td>
<td>16.32</td>
<td>12</td>
<td>14.36</td>
<td>f (pH, Pressure)</td>
</tr>
</tbody>
</table>

*Scandium rejections are assumed as the average of the other REEs rejections.
3.5.4. Electrochemical deposition economic model

This chapter reports the assumptions and schematic of the electrochemical deposition step. Afterwards, the costs and returns equations developed for this specific project are explained. Finally, the parameters used in the models are summarized.

The ECD step cost model has been developed with the following assumptions:

- SWNF concentrate is the feed for ECD step composed by seven filters in series with an increasing applied voltage. Each element is oxidized and separated from the stream when the applied voltage is equal or higher than its standard redox potential.
- Feed flow rate is assumed constant for each filter, equal to the NF concentrate flow rate.
- Capital costs and operating costs considered are due to ECD membrane and energy consumption, function of applied voltage, respectively.
- Treatment returns are due to the selling of pure Rare Earth Oxides (REOs) (including scandium that has not been experimented), according to the 2016 REOs sell prices.
- Operating costs and returns for the last filter are not considered if the products sale provides an economical return that is lower than the operating costs needed for its separation.

The above reported assumptions are summarized in the schematic of Figure 3.16.

Figure 3.16. Electrochemical deposition schematics considered in the cost model.
The electrochemical deposition economic model considers the capital costs due to the membranes used for the oxidation. The membrane area required to treat the NF concentrate flow rate depends on the ECD membrane flux and can be calculated with Equation 3.10.

$$A_{\text{mem,ECD}} = \frac{Q_{\text{f,ECD}}}{J_{ECD}} \tag{3.10}$$

where:
- $A_{\text{mem,ECD}}$: required membrane area per stage [m²]
- $Q_{\text{f,ECD}}$: ECD feed flow rate [m³/s]
- $J_{ECD}$: ECD permeate flux [m³/(m²·s)]

The total membrane capital cost can be calculated by multiplying the stage membrane area for the specific membrane cost, $C_{\text{mem,ECD}}$, and the number of stages, $n_{\text{stage}}$, used for the recovery, as reported in Equation 3.11.

$$\text{Cap_cost}_{ECD} = A_{\text{mem,ECD}} \cdot C_{\text{mem,ECD}} \cdot n_{\text{stage}} \tag{3.11}$$

The electrochemical deposition economic model considers operating costs due to energy consumption and the economic returns due to REEs oxides selling. The annual energy consumed by each ECD stage depends on the specific energy consumption, function of the applied voltage, and the ECD feed flow rate. The energy cost is proportional to the energy consumption according to the specific cost per kWh. The above explanations are summarized in Equations 3.12 and 3.13:

$$E_{\text{Cons,i}} = E_{\text{spec,i}} \cdot Q_{\text{f,ECD}} \cdot 3600 \cdot 24 \cdot 365 \tag{3.12}$$

where:
- $E_{\text{Cons,i}}$: annual energy consumption required by ECD stage i [kWh/year]
- $E_{\text{spec,i}}$: specific energy consumption for ECD stage i [kWh/m³]
- $Q_{\text{f,ECD}}$: ECD feed flow rate [m³/s]

$$E_{\text{Cost,i}} = E_{\text{Cons,i}} \cdot C_{\text{kwh}} \tag{3.13}$$

where:
- $E_{\text{Cost,i}}$: annual energy cost for ECD Stage i [$/year]
- $C_{\text{kwh}}$: specific energy price [$/kWh]

The annual amount of Rare Earth Oxides (REOs) recovered and sold is proportional to their concentrations in the NF concentrate stream, its flow rate and the ECD stage capture efficiency for each element.
The economic return resulting depends on the REOs selling prices in 2016. The above explanations are summarized in Equations 3.14 and 3.15:

\[
\text{Prod}_i = \frac{C_{c,i}}{1000} Q_f \cdot \frac{\text{REO}_i}{\text{REE}_i} \cdot \eta_i \cdot \frac{3600 \cdot 24 \cdot 365}{100} \quad (3.14)
\]

where:
- \(\text{Prod}_i\): element \(i\) oxide annual production \([\text{kg/year}]\)
- \(C_{c,i}\): element \(i\) concentration in the NF concentrate stream \([\text{g/m}^3]\)
- \(\eta_i\): ECD stage \(i\) capture efficiency for element \(i\) \([\%]\)
- \(\frac{\text{REO}_i}{\text{REE}_i}\): mass ratio of Rare Earth Oxide and Rare Earth Element \(\text{g}_{\text{REO}}/\text{g}_{\text{REE}}\)

\[
\text{Ann}_{\text{sell},i} = \text{Prod}_i \cdot \text{Sell}_{\text{price},i} \quad (3.15)
\]

where:
- \(\text{Ann}_{\text{sell},i}\): annual economical return for element \(i\) selling \([\$/\text{year}]\)
- \(\text{Sell}_{\text{price},i}\): element \(i\) specific selling price \([\$/\text{kg}]\)

The list of parameters used in the electrochemical deposition system cost model for each stage are reported in Table 3.14 with their units and values.

**Table 3.14.** ECD economic model parameters for each stage.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit of measure</th>
<th>Stage 1</th>
<th>Stage 2</th>
<th>Stage 3</th>
<th>Stage 4</th>
<th>Stage 5</th>
<th>Stage 6</th>
<th>Stage 7</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxidized elements</td>
<td>Fe, Si, Al</td>
<td>Eu</td>
<td>Sc</td>
<td>Tb</td>
<td>Dy</td>
<td>Er</td>
<td>Y</td>
<td></td>
</tr>
<tr>
<td>Standard ReDox potential</td>
<td>V &lt; = 1.66</td>
<td>1.99</td>
<td>2.09</td>
<td>2.28</td>
<td>2.30</td>
<td>2.33</td>
<td>2.37</td>
<td></td>
</tr>
<tr>
<td>Applied voltage</td>
<td>V 1.66</td>
<td>1.99</td>
<td>2.09</td>
<td>2.28</td>
<td>2.30</td>
<td>2.33</td>
<td>2.37</td>
<td></td>
</tr>
<tr>
<td>Flux</td>
<td>LMH 12</td>
<td>12</td>
<td>12</td>
<td>12</td>
<td>12</td>
<td>12</td>
<td>12</td>
<td></td>
</tr>
<tr>
<td>Specific membrane cost</td>
<td>$/m^2 107</td>
<td>107</td>
<td>107</td>
<td>107</td>
<td>107</td>
<td>107</td>
<td>107</td>
<td></td>
</tr>
<tr>
<td>Specific energy</td>
<td>kWh/m^3 2.27</td>
<td>5.67</td>
<td>5.67</td>
<td>5.67</td>
<td>5.67</td>
<td>5.67</td>
<td>5.67</td>
<td></td>
</tr>
<tr>
<td>Capture Efficiency</td>
<td>% 100</td>
<td>95</td>
<td>95</td>
<td>95</td>
<td>95</td>
<td>95</td>
<td>95</td>
<td></td>
</tr>
<tr>
<td>Product element purity</td>
<td>% /</td>
<td>&gt;99</td>
<td>&gt;99</td>
<td>&gt;99</td>
<td>&gt;99</td>
<td>&gt;99</td>
<td>&gt;99</td>
<td></td>
</tr>
<tr>
<td>Sell Price</td>
<td>$/kg 56.1</td>
<td>4200</td>
<td>394.69</td>
<td>178.53</td>
<td>23.98</td>
<td>3.17</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
3.6. Software for data analysis

Excel has been used for pre-treatment, water permeability and nanofiltration tests data analysis. This software permitted the calculations of pre-treatment efficiency, pure water membrane permeability, permeate flux and recovery, major elements and REEs rejections.

Minitab 17 helped the construction of the Design of Experiments for the nanofiltration tests. This software indicated the number and order of experiments to be performed with different combinations of operating parameters. The mathematical model correlating the responses of the NF performance calculated with Excel (permeate flux, REEs rejections) to the operating parameters (membrane, feed pH, pressure), have been developed by this software.

The economic model, including the NF step optimization study, has been developed on Matlab_R2016b. The performance models resulting from Minitab 17 have been reported in the economic model in Matlab. The Matlab surface fitting tool have been used to correlate the final specific gain to the operating parameters (nanofiltration feed pH and pressure) and a Matlab code has been created to find the maximum in the gain function to optimize the NF process operating parameters.

3.7. Bibliography

Chapter 4 - Results

This chapter focuses on the processing of the data collected during the experimental work, their inclusion in the economic model and the description of the results obtained. First of all, chapter 4.1 illustrates the synthetic leachate characteristics and the data collected in the pretreatment tests, including pH adjustment and pre-filtration steps, whose results have been used for the definition of the experimental plan of the second research phase and the implementation of the economic model. Chapter 4.2 reports the results of preliminary tests for the nanofiltration membrane characterization, necessary for the elaboration and interpretation of the results obtained in the cross-flow nanofiltration tests. In chapter 4.3 and 4.4, it is firstly explained the definition of the cross-flow nanofiltration experimental plan; then, the results from nanofiltration tests carried out on the synthetic NF feed with different membranes and operating conditions (pH and applied pressure) are presented with the evidences observed during the tests. The data obtained have been elaborated to assess the performance and efficiency of the membranes as function of operating conditions and implemented in the economic model. Chapter 4.5 shows the outcomes of the economic model developed and the criteria supporting the choice of the optimum operating conditions for the NF step. The test performed on the real leachate through the optimized processes is shown in chapter 4.6. Finally, fouling analysis on the material rejected by the NF membranes as function of the NF feed pH and leachate is reported in chapter 4.7.

4.1. Synthetic leachate features and pretreatment tests

A synthetic leachate recipe has been defined to uniform and easily compare the results of different recovery technologies. This recipe has been defined as the average composition of four real leachate samples. Using 1 % v/v HNO₃ the synthetic leachate pH is 0.95. The major elements and REEs concentrations are reported in Table 4.1.

<table>
<thead>
<tr>
<th>Element</th>
<th>Synt leachate Conc (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium (Na⁺)</td>
<td>6269.22</td>
</tr>
<tr>
<td>Magnesium (Mg²⁺)</td>
<td>10.24</td>
</tr>
<tr>
<td>Calcium (Ca²⁺)</td>
<td>32.61</td>
</tr>
<tr>
<td>Aluminum (Al³⁺)</td>
<td>270.98</td>
</tr>
<tr>
<td>Iron (Fe³⁺)</td>
<td>89.71</td>
</tr>
<tr>
<td>Silicon (Si)</td>
<td>593.22</td>
</tr>
<tr>
<td>REEs (Tb³⁺, Dy³⁺, Er³⁺, Eu³⁺, Nd³⁺, Y³⁺)</td>
<td>0.15</td>
</tr>
</tbody>
</table>
It can be noticed that major elements concentrations are from two to four orders of magnitude higher than REE concentrations. High sodium concentration is not seen as a big issue in nanofiltration since it is a monovalent ion that is reasonably well transmitted through the nanofiltration membrane (Bowen et al., 2002). Silicon in acidic solutions, depending on the pH and redox potential of the solution, is present as free trivalent cation or bounded with oxygen forming SiO₂ or SiO₄ (Kim et al., 2012), that are uncharged molecules rejected by NF only for sieving effect. The attention must be focused on the high concentrations of trivalent co-ions, such as iron and aluminum. In fact, the goal of the membrane separation step inside the whole REEs recovery line experimented in the project is to concentrate REEs present in the leachate and enhance their purity in the retentate stream produced and sent to the next step. The nanofiltration membrane can concentrate trivalent ions, such as REEs, rejecting them in the retentate and allowing a REE-poor flow to pass through the membrane. On the other hand, nanofiltration is not selective for REEs in presence of other trivalent co-ions, resulting in a limited enhancement of REEs purity from the NF feed to the retentate.

To lower the trivalent co-ions concentration in the feed sent to the nanofiltration step and to better control its fouling, that is one of the main issues especially for spiral wound membranes, a pretreatment step needs to be designed and optimized. The experimented pre-treatment step involves:

- pH adjustment: the pH is increased to the optimal value for co-metals precipitation without REEs loss. The pH increase is beneficial for the NF process as well, because leachate low pH can damage the NF membrane and decrease its life duration.
- Pre-filtration: separation of solids and precipitated co-metals from the main stream.

### 4.1.1. pH Adjustment

The initial synthetic leachate pH of 0.95 was increased in 13 bottles to values ranging from 1.5 to 5, to evaluate the occurrence of each element precipitation at different pH values. The resulting precipitates formed in the pH adjusted synthetic leachate are shown in Figure 4.1.
From the visual analysis of the bottles it can be stated that no visible changes occurred increasing the pH until 2.75. From pH 3.0 the yellowish color of the solution suggests iron oxidation without precipitation until a pH value of 3.5 where the yellow color is supplemented by visible precipitates at the bottom of the bottle. The precipitates amount increases with the pH and a whiter color of the precipitates reveals aluminum and silicon precipitations are occurring in addition to iron one. To support the visual analysis and to perform a first screening on the pH range to be evaluated in the next optimization experiments, the concentration of each element in the supernatant has been measured. Figure 4.2 reports the ratio between the concentrations of the elements dissolved in the supernatant and the feed synthetic leachate concentration as function of the pH.
It can be noticed that the visual evidences are confirmed for iron that starts to precipitate at pH 3.5 with a rapid decrease with the pH increase, becoming almost null at pH 4.5. Silicon starts to precipitate at pH 3.5 with a residual concentration almost 23% of the initial one at pH 5. Aluminum precipitates at 3.75 and rapidly decreases with the pH, becoming almost null at pH 4.5. Bivalent co-ions, such as magnesium and calcium don’t precipitate having the same concentration until pH 4.5. REEs loss starts at pH 4.0, reaching a supernatant concentration equal to 70% and 40% of the initial one at pH 4.5 and 5.0, respectively. This is probably due to REEs adsorption on the aluminum and iron silicate precipitates, rather than for REEs chemical precipitation. Since no precipitation occurs before pH 3.25, and due to the loss of almost one third of the REE at pH 4.5, the pH range investigated in the next experiments, aimed at the optimization of both the pre-treatment steps, goes from 3.25 to 4.25.

4.1.2. Pre-filtration

The pre-filtration has been carried out on the pH adjusted synthetic leachate to optimize the pre-treatments. The following factors have been optimized with this set of experiments: the pH at which the leachate is firstly adjusted, the pore size of the pre-filter and the precipitation time occurring between the pH adjustment and the pre-filtration.

Four filters pore sizes have been analyzed: 0.22 μm, 0.45 μm, 0.8 μm, 1 μm.

The optimal pre-filter pore size has been determined as the maximum that provides the complete rejection of the generated precipitates. It is important to make sure that all
the precipitates are rejected by the pre-filter to avoid fouling issues to the NF membrane. The optimum pore size has been selected, among the ones who can guarantee this requirement, as the biggest one so that it allows the maximum permeate flux and consequently smaller filter area and lower capital costs. The weights of the rejected precipitates generated filtrating 5 ml of pH adjusted synthetic leachate with different filter pore sizes are reported in Table 4.2 as function of pH.

**Table 4.2.** Separated precipitates weight (mg) as function of pH and filter pore size.

<table>
<thead>
<tr>
<th>Initial pH</th>
<th>Pore size 0.22 μm</th>
<th>Pore size 0.45 μm</th>
<th>Pore size 0.8 μm</th>
<th>Pore size 1 μm</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.25</td>
<td>9.0 ± 0.31</td>
<td>9.3 ± 0.22</td>
<td>5.2 ± 0.31</td>
<td>1.1 ± 0.11</td>
</tr>
<tr>
<td>3.50</td>
<td>10.6 ± 0.33</td>
<td>10.8 ± 0.21</td>
<td>6.0 ± 0.33</td>
<td>2.9 ± 0.10</td>
</tr>
<tr>
<td>3.75</td>
<td>14.7 ± 0.25</td>
<td>15.2 ± 0.24</td>
<td>10.2 ± 0.28</td>
<td>7.2 ± 0.14</td>
</tr>
<tr>
<td>4.00</td>
<td>18.5 ± 0.28</td>
<td>18.8 ± 0.21</td>
<td>15.1 ± 0.35</td>
<td>7.1 ± 0.07</td>
</tr>
<tr>
<td>4.25</td>
<td>23.6 ± 0.34</td>
<td>24.0 ± 0.23</td>
<td>17.9 ± 0.37</td>
<td>11.5 ± 0.09</td>
</tr>
</tbody>
</table>

The precipitates weight increases with the pH, independently from the filter pore size. This is in accordance with the decreasing dissolved concentrations shown in Figure 4.2. Secondly, it can be noticed that the precipitate weight increases decreasing the filter pore size, from 1 μm to 0.45 μm. Lowering the filter pore size to 0.22 μm does not provide an additional precipitates separation. This means that the optimal pore size can be selected at 0.45 μm corresponding to a microfiltration membrane.

Five precipitation times between pH adjustment and pre-filtration have been analyzed: 0, 20, 40, 60, 90 min.

The optimum precipitation time has been evaluated looking at the increase in elements removal efficiency in the period between two subsequent investigated precipitation times. The optimum has been chosen as the minimum precipitation time that provides the highest major elements removal efficiency increase with the lowest REEs loss. In fact, if the main precipitation effect occurs instantaneously, the pH is adjusted in-line and there is no need for a precipitation tank, reducing the capital costs. Increasing the precipitation time required, the needed tank volume and the resulting capital cost enhance.

The precipitation time effect on the pre-treatment performance has been studied calculating the pre-treatment removal efficiencies for each element "i" at different time intervals between pH adjustment and pre-filtration. Figure 4.3 represents the ratio between the element concentration in the pre-filtrated stream and the synthetic
leachate concentration as function of time, considering that data have the same trend with time for all the pH values tested.

![Figure 4.3](image.png)

**Figure 4.3.** Precipitation time effect on pre-filtration efficiency (pH=4).

It can be observed that there is no significant time effect on precipitation. In fact, the major trivalent co-ions precipitation occurs instantaneously. A further precipitation happens for Si and Al, after 20 minutes. On the other hand, the REEs purity doesn’t improve since after 20 minutes an additional loss of REEs decreases their amount at less than 85% of the initial leachate concentration. As consequence of the high REEs loss and the additional capital costs associated to the needed precipitation tank, an in-line precipitation has been selected as the optimum design for the pH adjustment step. The feed pH effect on the pre-treatment performance has been studied calculating the pre-treatment removal efficiencies for each element and the REEs purity in the permeate stream at different pH values. The optimal pH has been chosen as the one resulting in the highest major elements removal efficiency with the highest REEs purity and limited REEs loss. Figure 4.4 represents the percentages of the synthetic leachate concentrations that stay dissolved in the filtrated stream after pH adjustment and instantaneous pre-filtration at 0.45 μm as function of the pH for the trivalent co-ions (Al and Fe), Si and REEs.
Figure 4.4. Effect of pH on the dissolved filtrate stream concentrations compared to the initial synthetic leachate concentration.

From this graph, it can be observed that REE concentration in the filtrated stream is almost constant at 92% of the leachate one until pH equal to 3.75. An increase of pH at 4.00 results in an addition precipitation of the trivalent co-ions with a further REE loss of 4%. Adjusting the pH at 4.25 would result in the loss of almost 25% of the REE amount, that is not economically feasible. So, the optimum pH choice is restricted to the values of 3.75 and 4.00, whose elements concentrations are reported in Figure 4.5.

Figure 4.5. Major elements concentration (mg/L) and REEs concentration (μg/L) in the feed synthetic leachate, in the filtrated streams after pH adjustment at 3.75 and 4.00.

Figure 4.5 underlines that silicon and aluminum additional decrease going from pH 3.75 to 4.00 is relevant compared to the loss of REE. This results in an increase of REEs
purification from 0.12 to 0.15% of the total element amount in the filtrated stream going from pH 3.75 to 4.00. This result leads to the choice of 4.00 as the optimal pH for the initial pH adjustment. Adjusting the pH to 4.00, almost 98% and 41% of the leachate iron and silicon amounts are removed by pre-treatment, respectively. The aluminum amount is halved. Pre-treatment REEs removal is equal to 12%. Pre-treatments don’t have an influence on sodium, calcium and magnesium amount.

It must be clarified that, after pH adjustment to 4.00 and chemical precipitation, due to the filtration of the generated precipitates, the pH of the filtrated stream decreases from 4 to 3.5. The optimal pre-treatment removal efficiency and the resulting NF feed characteristics are summarized in Table 4.3.

<table>
<thead>
<tr>
<th>Element</th>
<th>Pretreatment Efficiency (%)</th>
<th>NF Feed Concentration (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium (Na⁺)</td>
<td>0</td>
<td>6269.22</td>
</tr>
<tr>
<td>Magnesium (Mg²⁺)</td>
<td>0</td>
<td>10.24</td>
</tr>
<tr>
<td>Calcium (Ca²⁺)</td>
<td>0</td>
<td>32.61</td>
</tr>
<tr>
<td>Aluminum (Al³⁺)</td>
<td>50.5</td>
<td>134.06</td>
</tr>
<tr>
<td>Iron (Fe³⁺)</td>
<td>97.8</td>
<td>1.97</td>
</tr>
<tr>
<td>Silicon (Si)</td>
<td>41</td>
<td>349.81</td>
</tr>
<tr>
<td>REEs (Tb³⁺, Dy³⁺, Er³⁺, Eu³⁺, Nd³⁺, Y³⁺)</td>
<td>12</td>
<td>0.133</td>
</tr>
</tbody>
</table>

### 4.2. Nanofiltration membrane characterization

Before using the four commercial NF membranes for the synthetic leachate cross-flow filtration, they have been characterized in terms of membrane surface charge and zeta potential as function of pH and water permeability, according to the procedures explained in chapters 3.3.4 and 3.3.3, respectively. The results of the characterization tests are illustrated in the next chapters.

#### 4.2.1. Commercial NF membranes Zeta Potential

Membrane zeta potential (ZP) is a fundamental parameter that indicates the sign and density of the membrane surface charge. As explained in chapter 2.3.2, the more positive is the ZP, the higher is the positive charge density on the membrane surface, thus the cations rejection. Since our target ions, the REEs, are trivalent cations, it is important to measure the IEP and zeta potential of the NF membranes selected to verify that they are positively charged in the studied pH range, that is between 1.5 and 3.5. The measured ZP for the four selected NF membranes as function of the electrolyte pH is reported in Figure 4.6.
Figure 4.6. Zeta potential as function of the electrolyte (0.1 M KCl) pH for four commercial NF membranes (NP010, NP030, DK, Duracid).

It can be noticed that the two PES membranes, NP010 and NP030, have similar IEP, at pH almost 3.3 and 3.2, respectively. Except for the experiments performed at pH 3.5, higher than their IEP, the two PES membranes are positively charged so they are expected to reject REEs. The other two thin-film membranes, DK and Duracid, have similar IEP at pH almost 4.2 and 4.3, respectively. Since their IEP is higher than 3.5, DK and Duracid membranes are supposed to reject REEs in the whole studied pH range. Looking at the ZP curves trends in the pH range between 2.5 and 3.5, we expect REEs rejection to be the lowest for NP010 and the greatest for DK.

4.2.2. Commercial NF membranes water permeability
Membrane water permeability is a fundamental parameter that relates the applied pressure to the membrane permeate flux. Higher water permeability results in higher membrane flux, at constant applied pressure, and means a greater flux fluctuation with pressure changes, as explained in Equation 2.2. With NP water, we do not expect ions to be present in the flow passing the NF membrane. Therefore, no osmotic pressure difference, $\Delta \pi$, occurs. Equation 2.2 in this test is transformed into Equation 4.1.

$$J_v = L_p \Delta P$$ (4.1)

The results of water permeability tests are shown in Figure 4.7, where measured NP water flux is reported as function of the applied pressure. According to Equation 4.1, the trend lines are forced to pass through the axis origin. The values of NP water permeability, $L_p$, and their estimation $R^2$ for each membrane are reported in Table 4.4.
Figure 4.7. NP water flux through the membrane as function of the applied pressure for four commercial NF membranes (NP010, NP030, DK, Duracid).

Table 4.4. NP water permeability for four commercial NF membrane.

<table>
<thead>
<tr>
<th>Membrane</th>
<th>NP010</th>
<th>NP030</th>
<th>DK</th>
<th>Duracid</th>
</tr>
</thead>
<tbody>
<tr>
<td>NP water permeability, $L_p$ (LMH bar$^{-1}$)</td>
<td>8.68</td>
<td>3.49</td>
<td>3.72</td>
<td>1.01</td>
</tr>
<tr>
<td>$R^2$</td>
<td>0.9284</td>
<td>0.9881</td>
<td>0.9179</td>
<td>0.9828</td>
</tr>
</tbody>
</table>

Water permeability tests illustrate that, as in Equation 4.1, NP water flux trend with the applied pressure is well described by a linear function with intercept in the axis origin. This is demonstrated by the high $R^2$ values, more than 0.91 for all the four models. In addition, NP010 has the highest NP water permeability, eight times the Duracid $L_p$ value. DK is slightly more water permeable than NP030, with an intermediate value between Duracid and NP010. NP water permeability is useful to characterize the membranes, but synthetic leachate membranes permeability is one of the main parameters to be evaluated for the NF performance and feasibility assessment. This is illustrated in chapters 4.3 and 4.4.

4.3. NF tests results for membrane selection

To design the nanofiltration step for REEs recovery three parameters have been optimized: the NF membrane used, NF feed pH and the pressure applied to the filtration system. Two separate experimental design plans were prepared: one for the
membrane selection and one for the pH and pressure conditions optimization. The following chapter, focuses on the membrane selection.

The first experimental plan for the pre-treated leachate NF tests has been prepared with the DoE methodology to identify the best performing NF membrane, among the four investigated, reducing the number of experiments. Nanofiltration membranes performance has been evaluated in terms of permeate flux and REEs rejection. Permeate flux highly depends on the applied pressure and on membrane permeability. It has been shown in chapter 4.2.2 that the four membranes have different water permeability values, therefore their permeate flux trends with pressure have different slopes. As a consequence, we can state that choosing a lower pressure the permeate fluxes of the four membranes would be less different than choosing a higher pressure value.

REEs rejection highly depend on the membrane surface zeta potential, that is function of the pH. In chapter 4.2.1, it has been clarified that the zeta potential trend as function of pH is different for the four membranes. In particular, since we do not have ZP measurements below pH 3.0, we cannot predict which membrane has the highest ZP and the most relevant expected REEs rejection in the whole investigated pH range.

In addition to the main effects of pressure and pH on NF membrane performance, we wanted to investigate their interaction effects, since no scientific evidences have been demonstrated in the literature on their combined influence on NF performance on ions separations.

To reduce the number of experiments needed for the membrane selection, achieving the maximum information, a two-level full factorial design, shown in Table 3.5, was identified as the most appropriate for the following reasons:
- Choosing to select the optimal membrane based only on one combination of pressure and pH would have counterfeited the choice according to the values selected.
- A two-level full factorial design for each of the four membranes allows to achieve resolution V, assessing main effects and all two-interaction effects, with 16 experiments.
- Choosing a three-level full factorial design more information on non-linear effects would have been detected, requiring 36 experiments to achieve resolution V. Non-linear effects are not supposed to alter significantly the membrane choice. Therefore, the additional information achieved with a three-level design are not counterbalanced by the experiments cost increase.
The choice of NF membranes, pressure and pH to be investigated has been based on different criteria.

The four NF membranes selected are suggested by their manufacturers for metals recovery, that is the aim of this study. They have been previously investigated for ions separation showing good performance in a pressure range from 12 to 40 bar and pH values between 3 and 10 (Artug et al., (2007); Niewerch et al., (2008); Aydiner et al., (2010); Gonder et al., (2011); Vergili et al., (2011); Hepsen et al., (2012)).

The pressure values selected (12 and 24 bar) have been chosen as the best for this study for two main reasons: lowering the pressure under 12 bar, the pre-treated leachate permeation through the membranes was hard to achieve and not constant over time. The cross-flow NF system used in this study was constituted by pipes allowing a maximum pressure of 30 bars. Therefore, 24 bar was selected as the maximum pressure to avoid laboratory safety risks.

The maximum pH was set to 3.5, that is the pre-treated leachate pH. Increasing the pH over 3.5 is not considered a good choice as it results in elements precipitation on the NF membrane surface with fouling issues.Decreasing the pH, higher REEs rejection is expected, as explained in chapter 2.3.2. The minimum pH was selected at 1.5, because a too acidic solution would have caused membrane damages and worse performance.

The membrane selection has been carried out choosing the most economically feasible system. The link between the NF performance and its feasibility used for the membrane selection is summarized in the following analysis:
- Higher permeate flux results in a smaller required membrane area, that leads to lower membrane and system components capital costs.
- Higher REEs rejection results in better REEs recovery, that provides an increased economic return, due to REEs sale.

The NP water and pre-treated leachate permeate flux through the four NF membranes as function of pressure and pH are shown in Figure 4.8.
A decrease in permeate flux occurred when the pre-treated leachate, containing ions, is filtrated instead of NP water. This is due to a decrease in permeability, $L_p'$, and to the effect of the osmotic pressure difference generated by the difference in ions concentration on the two sides of the membrane. The pre-treated synthetic leachate NF membranes permeabilities are reported in Table 4.5 as function of pH.

**Figure 4.8.** NP water and pre-treated leachate permeate flux for four membranes (NP010, NP030, DK, Duracid) as function of applied pressure and feed pH.
Table 4.5. Pre-treated synthetic leachate permeability, $L_p'$, for the four commercial NF membranes as function of feed pH.

<table>
<thead>
<tr>
<th>Membrane</th>
<th>NP010</th>
<th>NP030</th>
<th>DK</th>
<th>Duracid</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH=1.5 leachate permeability, $L_p'$ (LMH bar⁻¹)</td>
<td>4.50</td>
<td>0.71</td>
<td>0.67</td>
<td>0.27</td>
</tr>
<tr>
<td>pH=3.5 leachate permeability, $L_p'$ (LMH bar⁻¹)</td>
<td>0.85</td>
<td>0.74</td>
<td>0.46</td>
<td>0.23</td>
</tr>
</tbody>
</table>

As it was for NP water, also in case of pre-treated leachate, the highest permeability is measured for NP010, for both pH values. The less permeable membrane is Duracid. In the case of pre-treated leachate NP030 permeability is slightly higher than DK. These evidences can be due to the NF membranes pore size, that is proportional to the membrane weight cut off (MWCO). In fact, as reported in Table 3.4, NP010 and Duracid have the biggest and smallest MWCO, respectively. In addition to the pore size, permeability is influenced by the membrane thickness and effective porosity. In fact, the membrane displays a resistance effect on the permeation, increasing with its thickness and decreasing with its effective porosity, both related to the membrane material. This can be the reason of the higher leachate permeability for PES membranes compared to the thin-film ones. An additional resistance to permeation is provided by fouling on the membrane surface and inside the pores. So, PES membranes higher permeability could be due to lower fouling effect compared to the thin-film membranes. A significant decrease in permeability increasing the pH from 1.5 to 3.5 can be noticed only for NP010 (-81.1 %) and DK (-31.3 %) membranes. This is an index of the interaction between pH and pressure on NF membrane permeate flux.

The REEs rejection achieved by the four NF membranes as function of pressure and pH are shown in Figure 4.9.
The first important thing to be noticed is that NP010 and NP030 reject less than 15% of the REEs entering the system. This low rejection is probably caused by a combination of low positive membrane charge, as revealed by the low zeta-potential measure in this pH range and the high molecular weight cut off. The absence of both sieving and Donnan potential rejection mechanisms results in low REEs retentions. This means that they cannot be selected for REEs recovery and concentration.

Focusing on the other two membranes, it can be noticed that, in all the operating conditions combinations, DK performs a REEs rejection more than 10% higher than Duracid. This can be due to the higher ZP, as can be seen in Figure 4.6. According to the results of the first set of experiments, DK was selected as the best performing membrane for REE recovery due to its higher permeate flux and REEs rejection compared to Duracid, that result in a more economically feasible system.

4.4. NF tests results for operating conditions optimization

In this chapter, the definition of the Design of Experiments (DoE) used for operation conditions optimization is presented. The results of the pre-treated leachate NF tests for the DK membrane at different filtration operating conditions are reported along with two proposed performance models achieved with the tests. These models have been used to identify the optimal operating conditions combination for the NF step. Before selecting the best experimental design, few considerations on the expected relations between operating factors (pressure and pH) and performance parameters (permeate flux and REE rejection) must be reported. Quadratic effects of pH on ions rejections have been found by Artug et al. (2007) and Lee et al. (2014). The pressure effect on ions rejection highly depends on the solution to be treated; quadratic effect has been found by Abidi et al. (2016). The interaction effect of pH and pressure on permeate flux has been indicated for DK analyzing the results of the first set of experiments, in chapter 4.3.

Response Surface Methodology (RSM) has been selected as the most appropriate DoE technique because it can well predict quadratic main effects and the interaction effect of the two variables on the responses, and because it is useful for optimizing processes. RSM is a statistical modeling technique used to evaluate the relationship between the set of experimental factors (x_i) and observed response (Y). In this study, the experimental factors are the applied pressure and the feed solution pH, while the two observed responses are the permeate flux and REEs rejection.
The first step of the optimization process using a RSM is the selection of one of the three Central Composite Designs (see Chapter 2.4). Since the edge points of the two-level design used in the first set of experiment are located at the limits of the observation space that can be investigated, star points cannot be designed out of these limits for safety and operating issues, as explained in Chapter 4.3. Therefore, a central composite face-centered (CCF) design was performed adding the star and central points at the center of each face of the factorial space resulting in a three-level design, as reported in Table 3.6.

A preliminary analysis on the experimental data has been carried out to evaluate if the DK membrane rejection of each REE at different pH and pressure significantly depended by the specific REE analyzed. If there is no significant effect of the REE analyzed on DK performance, we can evaluate all the REEs rejections with a unique model in which the response is the average REEs rejection. The REEs rejections at different operating conditions combinations is reported in Table 4.6 and Figure 4.10.

**Table 4.6.** Average REE rejections (%) at different operating conditions combinations.

<table>
<thead>
<tr>
<th>Pressure</th>
<th>12</th>
<th>18</th>
<th>24</th>
<th>12</th>
<th>18</th>
<th>24</th>
<th>12</th>
<th>18</th>
<th>24</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Y</td>
<td>94.9</td>
<td>93.8</td>
<td>92.7</td>
<td>97.7</td>
<td>96.1</td>
<td>95.6</td>
<td>99.0</td>
<td>98.7</td>
<td>98.4</td>
</tr>
<tr>
<td>Nd</td>
<td>95.0</td>
<td>94.0</td>
<td>92.9</td>
<td>97.9</td>
<td>96.3</td>
<td>95.4</td>
<td>99.5</td>
<td>99.1</td>
<td>98.8</td>
</tr>
<tr>
<td>Eu</td>
<td>95.1</td>
<td>94.0</td>
<td>92.9</td>
<td>97.9</td>
<td>96.2</td>
<td>95.4</td>
<td>99.6</td>
<td>99.1</td>
<td>98.8</td>
</tr>
<tr>
<td>Tb</td>
<td>94.6</td>
<td>93.6</td>
<td>92.6</td>
<td>97.9</td>
<td>96.0</td>
<td>95.1</td>
<td>99.0</td>
<td>98.6</td>
<td>98.3</td>
</tr>
<tr>
<td>Dy</td>
<td>94.6</td>
<td>93.7</td>
<td>92.8</td>
<td>97.4</td>
<td>96.3</td>
<td>95.2</td>
<td>99.1</td>
<td>98.7</td>
<td>98.5</td>
</tr>
<tr>
<td>Er</td>
<td>95.1</td>
<td>94.2</td>
<td>93.4</td>
<td>97.9</td>
<td>96.5</td>
<td>95.4</td>
<td>99.6</td>
<td>99.2</td>
<td>98.9</td>
</tr>
</tbody>
</table>
It is possible to notice that all the REEs rejections have the same trend. To evaluate if there is a statistically significant effect of the REE selected on its rejection behavior, a one-way ANOVA has been performed on REEs rejections experimental data. A single factor or one-way ANOVA was used to test the null hypothesis that the means of several populations are all equal. If the ANOVA result provides an F value greater than the critical F value the null hypothesis is rejected, that means that populations are not all equal. If the ANOVA result provides a F value lower than the critical F value the null hypothesis is accepted, meaning that populations are all equally distributed. In this case F was equal to 0.135, lower than the F critical, 2.303. Therefore, the null hypothesis of equal distribution for all the REEs rejections has been accepted and one unique model considering the average between the REEs rejections has been built.

The full quadratic stepwise analysis, including all linear, quadratic and interaction effects of pressure and pH on the response, has been used for the terms selection, with a significance level, $\alpha$, of 0.05. The stepwise analysis resulted in the model described by Equation 4.2.

$$\text{REEs\_Rejection} = \beta_0 + \beta_1 \text{pH} + \beta_2 \text{Pressure} + \beta_{12} \text{pH} \text{Pressure}$$  \hspace{1cm} (4.2)

where pH (-) and Pressure (bar) represent the operating conditions experimented, while REEs\_Rejection is expressed as percentage. Pressure and pH influences on REEs rejection are both linear with no quadratic significant effect. The interaction between applied pressure and feed pH has also a significant effect on the rejection. It means that
the effect of pressure on REEs rejection depends on the level of pH. Table 4.7 reports the estimated coded and uncoded coefficients of the model and their p-values. The coded coefficients are estimated using factors’ levels values as more convenient values, equal for all the factors (low level = -1, center = 0, high level = 1). Coded units let you compare the size of the coefficients (on a common scale) to determine which factor has the largest impact on the response. The positive or negative values of the linear coefficients refer to the direct or inverse proportionality of the factors on the permeate flux. If $\beta_{12}$ is positive, then it means that the more positive pressure is, the more positive becomes the effect of pH on permeate flux. Conversely, if $\beta_{12}$ is negative, then the more positive pressure is, the more negative the effect of pH on permeate flux becomes. On the other hand, uncoded coefficients are estimated using factors’ levels values as the real values (e.g. pH: low level=1.5, center=2.5, high level=3.5). Therefore, uncoded coefficients are the real model predictors that must be considered when predicting the REEs rejection as function of the operating conditions.

<table>
<thead>
<tr>
<th>Predictor</th>
<th>Symbol</th>
<th>Coded Coeff.</th>
<th>Uncoded Coeff.</th>
<th>p-value</th>
<th>VIF</th>
</tr>
</thead>
<tbody>
<tr>
<td>Constant</td>
<td>$\beta_0$</td>
<td>96.289</td>
<td>95.11</td>
<td>0.000</td>
<td>1</td>
</tr>
<tr>
<td>pH</td>
<td>$\beta_1$</td>
<td>2.535</td>
<td>1.512</td>
<td>0.000</td>
<td>1</td>
</tr>
<tr>
<td>Pressure</td>
<td>$\beta_2$</td>
<td>-0.867</td>
<td>-0.2851</td>
<td>0.000</td>
<td>1</td>
</tr>
<tr>
<td>pH × Pressure</td>
<td>$\beta_{12}$</td>
<td>0.338</td>
<td>0.0563</td>
<td>0.027</td>
<td>1</td>
</tr>
</tbody>
</table>

The regression explains 96.01\% of the variance ($R^2 = 0.9601$, adjusted $R^2 = 0.9546$, predicted $R^2 = 0.9483$, Std. Error of the Estimate = 0.404). The p-values under $\alpha=0.05$ indicates that these predictors are significant. VIF values equal to 1 show that all the predictors are not correlated each other. Looking at the coded coefficient, it can be stated that the pressure linear coefficient is negative, indicating that the higher the pressure the less the DK membrane rejects REEs. The feed solution pH has a positive linear effect on REEs rejection, revealing a direct proportion between the two. The lower value for the pressure coded coefficient compared to the pH one demonstrates that the REE rejection is more influenced by feed pH changes. The interaction effect is positive. The outcomes of the uncoded coefficients estimates are well shown in Figure 4.12 where the experimental measurements (points) and the fitted model (curve or lines), are drawn in a 3-dimensional and 2-dimensional spaces, as function of pressure and pH.
The built model trend as function of the feed solution pH has opposite inclination than the zeta potential curve of the DK membrane, shown in Figure 4.6. This means that, although the membrane surface positive charge density is supposed to increase with pH decrease, no cations rejection enhancement occurs. This can be based on Ong et al. (2002) theory suggesting that increased solution ionic concentration also increases ion concentration on membrane surface therefore reducing its Donnan potential, “shielding” solutions counter-ions from membranes repulsion with a resulting increased ion permeation. In fact, adding HNO3 to the feed solution to decrease the initial pH of 3.5 to 2.5 and further to 1.5, the ionic concentration has increased, as demonstrated by the increasing solution conductivity with pH decrease, in Table 4.8.


Since the solution conductivity is high, considering that sea salt conductivity is around 54 mS/cm, the reduced Donnan potential effect seems to be a good scientific explanation of the DK performance on pre-treated leachate.

The model result suggests that the maximum REEs rejection occurs when filtration is performed at minimum pressure and maximum pH. Thus, looking only to REEs rejection, a pressure of 12 bar and pH 3.5 would be chosen as the optimal operating conditions. Anyway, the pre-treated leachate permeate flux has also to be considered for the selection of the operating parameters.

Therefore, permeate flux values resulting from the experiments have been used to build a model as function of the applied pressure and NF feed pH. The same full quadratic stepwise analysis used for REEs rejection model, has been performed on permeate flux data. The stepwise analysis resulted in the model described by Equation 4.3.

\[
\text{Flux} = \beta_0 + \beta_1 \text{pH} + \beta_2 \text{Pressure} + \beta_{11} \text{pH}^2 + \beta_{12} \text{pH Pressure}
\]  

(4.3)

where Flux is expressed in LMH. Pressure influence on permeate flux is linear with no quadratic significant effect. The feed solution pH has a linear and quadratic effect on the permeate flux. The interaction between applied pressure and feed pH has a significant effect on the permeate flux. It means that the effect of pressure on permeate flux depends on the level of pH, so the permeability value Lp is function of the feed solution pH. Table 4.9 reports the estimated coded and uncoded coefficients of the model and their p-values. The quadratic coded coefficient indicates which way the curve is bending: a positive value indicates a convex curve (apex at the bottom) while concave curve (apex at the top) has a negative value.

<table>
<thead>
<tr>
<th>Predictor</th>
<th>Symbol</th>
<th>Coded Coeff.</th>
<th>Uncoded Coeff.</th>
<th>p-value</th>
<th>VIF</th>
</tr>
</thead>
<tbody>
<tr>
<td>Constant</td>
<td>(\beta_0)</td>
<td>22.222</td>
<td>0.54</td>
<td>0.000</td>
<td>1</td>
</tr>
<tr>
<td>pH</td>
<td>(\beta_1)</td>
<td>-1.489</td>
<td>8.20</td>
<td>0.000</td>
<td>1</td>
</tr>
<tr>
<td>Pressure</td>
<td>(\beta_2)</td>
<td>3.761</td>
<td>0.8502</td>
<td>0.000</td>
<td>1</td>
</tr>
<tr>
<td>(\text{pH}^2)</td>
<td>(\beta_{11})</td>
<td>-1.616</td>
<td>-1.616</td>
<td>0.000</td>
<td>1</td>
</tr>
<tr>
<td>(\text{pH}\times\text{Pressure})</td>
<td>(\beta_{12})</td>
<td>-0.536</td>
<td>-0.0894</td>
<td>0.011</td>
<td>1</td>
</tr>
</tbody>
</table>
The regression explains 97.24% of the variance ($R^2 = 0.9724$, Adjusted $R^2 = 0.9671$, predicted $R^2 = 0.9515$, Std. Error of the Estimate = 0.5399). These predictors are significant and not correlated each other. Looking at the coded coefficient, it can be stated that the pressure linear coefficient is positive, indicating that the higher the pressure the more permeable is the DK membrane. The feed solution pH has a negative linear effect on the flux, revealing an inverse proportion between the two. In addition, the permeate flux has a quadratic concave trend with the pH. The higher value for the pressure coded coefficient compared to the pH one demonstrates that the permeate flux is more influenced by pressure changes. The interaction effect is negative, therefore higher the pressure, the more negative the effect of pH on permeate flux becomes. The outcomes of the uncoded coefficients estimates are shown in Figure 4.11 where the experimental measurements (points) and the fitted model (curve or lines), are drawn in 3-dimensional and 2-dimensional spaces, as function of pressure and pH.

![Figure 4.11.](image-url)
The built model trend as function of the pressure can be well described by the Spiegler and Kedem equation (Eq 2.2) where the permeability coefficient is function of feed solution pH according to Equation 4.4:

$$L_p' = 0,8502 - 0,0894 \text{pH} \quad (4.4)$$

The pre-treated leachate permeability decreases linearly with the pH. One scientific explanation can be found in the effect of the feed pH on the “openness” of the membrane pores, that impacts on permeate flux (Mullet et al., 2014). In fact, according to Hagen-Poiseulle equation (Mohammad et al., 2007) permeability can be expressed as function of membrane pore radius ($r_{mp}$), as reported in Equation 4.5:

$$L_p = \frac{r_{mp}^2}{8 \mu_w \frac{\Delta x}{A_k}} \quad (4.5)$$

where $\mu_w$ is the solution viscosity and $\Delta x$ and $A_k$ are the membrane thickness and effective porosity, respectively. According to the results, the pH increase leads to DK membrane pore closure, reducing its permeability. Since no pore size measurements have been carried out in this study, further investigations are required to relate the feed solution pH to DK membrane pore size. In addition, the flux decrease with pH can be attributed to the higher ions rejection occurring at increasing pH. In fact, the more the ions are rejected, the higher is their membrane wall concentration at feed side, resulting in a higher osmotic pressure difference, main cause of flux decrease. The ions rejection results in membrane fouling on the surface and in the pore inlet, that apply two additional resistances to that of the bare membrane ($R_m$) on the solution flux, $J_v$: the cake formation resistance ($R_c$) on the membrane surface and the pore inlet resistance ($R_{in}$). This is illustrated in Equation 4.6 (Koyuncu et al., 2004):

$$J_v = \frac{\Delta P - \Delta \pi}{\mu R_{tot}} = \frac{\Delta P - \Delta \pi}{\mu (R_m + R_c + R_{in})} \quad (4.6)$$

The model results suggest that the maximum permeate flux occurs when filtration is performed at maximum pressure and minimum pH. Thus, looking only to flux, a pressure of 24 bar and pH 1.5 would be chosen as the optimal operating conditions. The flux study provides optimum operating conditions values opposite compared to the ones resulting from REEs rejection optimization. So, it is hard to select which one of the two performance responses is better to optimize, since no suggestions are provided
by the literature on which between permeate flux and rejection has a bigger impact on the recovery costs and gain.

Therefore, an economic model has been developed to optimize the NF operating conditions maximizing the gain achieved by the REEs recovery.

4.5. Economic model results

The cost model developed in a previous study (Sethi et al., 2001) has been applied and integrated to estimate capital and operating costs for real scale pre-treatment, nanofiltration and post-treatment processes.

The results are presented considering the following data, assumed by the project team, for a real scale REEs recovery system:

- coal ash mass flow rate entering the recovery plant: 1000 kgash/h;
- produced leachate flow rate: 3434.66 kgleachate/h (Taggart et al., 2016);
- leachate REEs concentrations: see Table 3.13 (Taggart et al., 2016).

This study experimental results integrated in the economic model are:

- NaOH dose (ml/l) for the first pH adjustment to increase the pH from 0.95 to 4;
- No need for precipitation tank, but in-line pH adjustment;
- Microfiltration as pre-filtration;
- HNO3 dose (ml/l) for the second pH adjustment to decrease the pH from 3.5 to the NF feed solution pH: 1.5, 2.5 or 3.5;
- DK specific cost per unit area (m²) of membrane surface;
- The built NF permeate flux model as function of pH and pressure;
- The built NF REEs rejection model as function of pH and pressure.

Inserting different pH and pressure combinations, in the developed economic model, annual capital and operating costs for pre-treatment (pH adjustments and microfiltration), nanofiltration and ECD steps have been estimated. Annual costs have been normalized to the annual mass of coal ash entering the recovery plant. Specific capital and operating costs ($/kgash) for the modeled recovery steps as function of the operating condition combinations are shown in Figure 4.12.
The total REE recovery specific cost varies from 0.017 to 0.023 $/kg$_{ash}$ changing pH and pressure in the analyzed ranges. Looking at the pre-treatments costs, including the two pH adjustment steps and the microfiltration, it can be noticed that the major cost contribution is due to the first pH adjustment to increase the pH from 0.95 to 4. In fact, the NaOH dose and specific cost is much higher than the HNO$_3$ ones. A feasibility study should be performed to assess if a NaOH recovery at the hand of the plant and recycling at the initial leaching step is less expensive than using always new NaOH. Due to its low energy and disposal costs, microfiltration major costs are the capital ones. As for the second pH adjustment by HNO$_3$ dosage, its costs and consequently the total pre-treatment costs decrease increasing the NF feed solution pH. Focusing on nanofiltration costs, the membrane area, capital costs and operating costs are reported in Table 4.10.

**Table 4.10.** NF membrane area, capital and operating costs at different operating condition combinations.

<table>
<thead>
<tr>
<th>pH</th>
<th>1.5</th>
<th>2.5</th>
<th>3.5</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH = 1.5</td>
<td>188.4</td>
<td>151.8</td>
<td>127.1</td>
</tr>
<tr>
<td>pH = 2.5</td>
<td>181.4</td>
<td>150.7</td>
<td>128.9</td>
</tr>
<tr>
<td>pH = 3.5</td>
<td>210.7</td>
<td>175.2</td>
<td>149.9</td>
</tr>
<tr>
<td>Pressure (bar)</td>
<td>12</td>
<td>18</td>
<td>24</td>
</tr>
<tr>
<td>Membrane Area (m$^2$)</td>
<td>60.38</td>
<td>54.06</td>
<td>49.44</td>
</tr>
<tr>
<td>Capital cost ($10^3$/year)</td>
<td>49.23</td>
<td>50.08</td>
<td>50.86</td>
</tr>
<tr>
<td>Operating cost ($10^3$/year)</td>
<td>0.005</td>
<td>0.02</td>
<td>0.025</td>
</tr>
<tr>
<td>Pressure (bar)</td>
<td>12</td>
<td>18</td>
<td>24</td>
</tr>
</tbody>
</table>

**Figure 4.12.** Specific capital and operating costs ($/kg$_{ash}$) for the modeled recovery steps as function of the operating condition combinations.
It can be noticed that the major cost contribution is due to the initial capital cost, 50 to 60% of the total specific NF costs. NF capital costs enhance increasing the pH from 1.5 to 3.5. This is due to the lower permeate flux performed at high pH, resulting in a bigger required NF membrane area. Membrane and all the other equipment capital costs increase with the membrane area, thus with higher pH. The opposite trend is highlighted for the effect of pressure on capital costs. In fact, increasing the pressure, permeate flux is enhanced, required membrane area and the resulting equipment capital costs are lower. NF operating costs increase with applied pressure and decrease with the pH. The higher NF operating cost at pH 1.5 compared to 3.5 is due to the acid (HNO3) dosage before NF. In fact, adding HNO3 to the pre-treated leachate the feed and permeate flow rates of the nanofiltration step are higher. Since the major contributor to operating cost is the NF permeate disposal, proportional to the permeate flow rate, higher operating costs are estimated for lower pH.

NF step has the highest costs in the modeled recovery line. In reality, this is due to the fact that ECD model considers only membrane and energy as capital and operating costs, respectively. Only these two costs have been considered in this study because they are the ones directly influenced by the NF operating conditions (pH and pressure) that we wanted to optimize with this economic model. A more detailed ECD economic model should be developed to state its feasibility and real contribution to the total REEs recovery costs. Looking at Figure 4.12, it can be seen that ECD capital cost decreases with the NF applied pressure. This is due to the fact that increasing the NF applied pressure, NF permeate flux increases, decreasing the concentrate flow rate. Since the concentrate flow rate, sent as feed at the ECD step, is lower for higher NF pressure, the required ECD surface area and related capital costs are lower. The same analysis can be applied to the decreasing operating costs with NF applied pressure. In fact, lower the concentrate flow rate sent to ECD step, less energy is required to guarantee the elements oxidation. The opposite trend is highlighted for the effect of pH on capital and operating ECD costs. In fact, increasing the pH, NF permeate flux is worsen and concentrate flow rate is enhanced. Thus, required ECD area and energy are higher.

To optimize the NF step operating conditions, the final gain has been chosen as the optimizing parameter. To calculate the gain, returns generated by Rare Earth Oxides (REOs) sales must be estimated. Specific REOs sale returns ($/kgash) divided by REE are reported in Figure 4.13 as function of the operating condition combinations.
Figure 4.13. Specific REO sale returns ($/kg ash) divided by REE as function of the operating condition combinations.

The total specific sale return varies from 0.278 to 0.297 $/kg ash changing pH and pressure in the analyzed ranges. Since these returns are always 1 order of magnitude higher than REEs recovery costs, the recovery line modeled is feasible, regardless the NF operating condition combination.

Looking at the returns trend, it can be noticed that it increases with the pH. This is due to the increasing REEs rejection and concentrate flow rate with the pH resulting in the enhancement of the REEs mass entering in the ECD process and being recovered, with an increased sale return. The opposite happens for increasing pressure that results in lower concentrate flow rate and so recovered REEs mass. As can be noticed from Figure 4.13, no sale returns are expected from neodymium (Nd). This is because its standard Redox potential is equal to sodium one. Therefore, designing an addition ECD stage to recover Nd, sodium would be simultaneously oxidized creating a product that is less than 1% pure in Nd, so impossible to be sold as pure REO. As can be noticed from Figure 4.13, almost all the sale returns are due to scandium oxide sale. In fact, scandium oxide recovered mass and specific sell price are the highest among the REOs. Figure 4.14 reports sale return of all the REOs, except scandium, as function of the operating condition combinations.
Figure 4.14. Specific REOs sale returns ($/kg Ash), excepted scandium, divided by REO, as function of the operating condition combinations.

From Figure 4.14 it can be better noticed that only in case pressure is set at 24 bar and pH 1.5 and 2.5 the yttrium recovery is feasible. The most important outcome of this analysis is that, if scandium is not recovered, the total REEs recovery specific sale return varies from 0.0044 to 0.0048 $/kg Ash changing pH and pressure in the analyzed ranges. Since these returns are always 1 order of magnitude lower than REEs recovery costs, the recovery line modeled is not feasible if scandium is not recovered, regardless the NF operating condition combination.

Considering the case with scandium recovery, the specific gain in $/kg Ash is calculated as the difference between the specific sale return and the recovery cost per kg of coal ash entering the modeled line. The results are shown in Figure 4.15, where the specific gain estimated with the model at the experimented pH and pressure values (points) and the fitted model (curve or lines), are drawn in a 3-dimensional and 2-dimensional spaces, as function of pressure and pH.
Figure 4.15. Specific gain ($/kg_{ash}$) calculated with the economic model (points) and fitted model (curve or lines), in a 3-dimensional (above) and 2-dimensional (below) spaces, as function of pressure (bar) and pH.

The specific gain varies from 0.260 to 0.276 $/kg_{ash}$ changing NF feed pH and applied pressure in the analyzed ranges. The specific gain increases with increasing pH. This is due to the fact that the sale return enhancement with the pH is higher than the specific recovery cost increase. The pressure effect on the specific gain is dependent on the pH value. For low pH the specific gain is inversely proportional to the pressure. At the maximum pH, the applied pressure appears not to have a significant effect on the specific gain. This is confirmed by the specific gain contour plot generated with the estimated data and fitting model, as function of pH and pressure, reported in Figure 4.16.
In fact, looking at Figure 4.16, at pH value of 3.5 the specific gain is estimated to be in the same range (0.274-0.276 $/\text{kg}_{\text{ash}}$), regardless the NF applied pressure. To evaluate if there is a statistically significant effect of pressure on specific gain, a one-way ANOVA has been performed on estimated specific gain data. In this case F is equal to 0.155, lower than the F critical, 5.14. Therefore, the null hypothesis of no statistically significant effect of pressure on specific gain is accepted.

The NF operating conditions optimization has been based on the specific gain analysis just presented. The optimal NF feed pH, that maximizes the specific gain is pH 3.5. Thus, no second pH adjustment is required in the recovery line. Since at pH 3.5, no significant effect of pressure appears on the specific gain, the pressure optimization in the analyzed range has been based on criteria other than the economic one. For safety reasons and to minimize the risk of high required maintenance for NF membranes, pump and the other system equipment, the lowest pressure, that is 12 bar, has been selected as the optimal one.

This optimization leads to choose the same operating conditions that would maximize the REEs rejection and minimize the NF permeate flux, as explained in chapter 4.4. It is therefore interesting to analyze the relations that REEs rejection and NF permeate flux have with the specific gain. The REEs rejection has a positive effect on the specific gain, as shown in Figure 4.17. This is due to the higher recovered REEs mass resulting from the enhanced REEs rejection.
The effect of NF permeate flux on the specific gain is the result of different mechanisms. The costs decrease with the flux. In fact, the capital costs of the nanofiltration and ECD steps decrease due to the lower required membranes area. In addition, operating ECD costs decrease with lower ECD feed flow rate at higher NF flux. On the other hand, increasing the NF permeate flux, the NF concentrate flow rate and the REEs mass that can be recovered with the following ECD step decrease. Therefore, enhancing the NF permeate flux, also the REOs sale returns decrease. Since this last decline is higher than the costs reduction, the specific gain tends to decrease with the NF permeate flux, as shown in Figure 4.18.

These results highlight that choosing the NF operating conditions that minimize the permeate flux, that is pH 3.5 and pressure 12 bar, optimizes the process from an economic point of view.
4.6. Real leachate optimized study

After the optimization of the whole pre-treatment and NF recovery steps with the synthetic leachate, one set of experiments has been performed on real leachate to simulate the optimized designed recovery line. Since the real leachate contained non-dissolved solids in it, a first 1 μm coarse filtration has been performed to separate them from the liquid phase of the leachate. After that, the optimized line has been tested, with the following steps:
- pH adjustment to increase the initial pH to 4;
- pre- filtration with 0.45 μm filter right after the pH adjustment;
- no second pH adjustment needed since the NF feed pH was already 3.5;
- cross flow nanofiltration with DK membrane at applied pressure of 12 bar.

The picture of the real leachate as it is and after the three pre-treatment stages is reported in Figure 4.19.

![Figure 4.19. Real raw leachate, coarse filtrated, pH adjusted and micro-filtrated leachate.](image)

As we can see the coarse filtration removed the solids present in the raw leachate. The leachate at pH 4.00 has a more intense orange color compared to the synthetic leachate at the same pH. This could be due to higher Fe/Al ratio in the real leachate compared to the synthetic leachate, that results in a more orange color of the precipitates. The raw leachate concentrations, the pre-treatment removal efficiency and the NF rejections for synthetic and real leachate are compared in Table 4.11.
Table 4.11. Raw leachate concentrations, the pre-treatment removal efficiency and the NF rejections for synthetic and real leachate.

<table>
<thead>
<tr>
<th>Element</th>
<th>Leachate Conc. (mg/L)</th>
<th>Pre-treatment Efficiency (%)</th>
<th>NF Rejection (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Synth. leachate</td>
<td>Real leachate</td>
<td>Synth. leachate</td>
</tr>
<tr>
<td>Na⁺</td>
<td>6269.22</td>
<td>5404.27</td>
<td>0</td>
</tr>
<tr>
<td>Mg²⁺</td>
<td>10.24</td>
<td>65.29</td>
<td>0</td>
</tr>
<tr>
<td>Ca²⁺</td>
<td>32.61</td>
<td>458.25</td>
<td>0</td>
</tr>
<tr>
<td>Al³⁺</td>
<td>270.98</td>
<td>249.32</td>
<td>50.5</td>
</tr>
<tr>
<td>Fe³⁺</td>
<td>89.71</td>
<td>98.06</td>
<td>97.8</td>
</tr>
<tr>
<td>Si</td>
<td>593.22</td>
<td>641.95</td>
<td>41</td>
</tr>
<tr>
<td>Y³⁺</td>
<td>0.15</td>
<td>0.401</td>
<td>12</td>
</tr>
<tr>
<td>Nd³⁺</td>
<td>0.15</td>
<td>0.438</td>
<td>12</td>
</tr>
<tr>
<td>Dy³⁺</td>
<td>0.15</td>
<td>0.069</td>
<td>12</td>
</tr>
<tr>
<td>Er³⁺</td>
<td>0.15</td>
<td>0.036</td>
<td>12</td>
</tr>
<tr>
<td>Eu³⁺</td>
<td>0.15</td>
<td>0.033</td>
<td>12</td>
</tr>
<tr>
<td>Tb³⁺</td>
<td>0.15</td>
<td>0.015</td>
<td>12</td>
</tr>
<tr>
<td>Sc⁵⁺</td>
<td>0</td>
<td>0.349</td>
<td>87.7</td>
</tr>
<tr>
<td>Uncritical REEs</td>
<td>0</td>
<td>0.773</td>
<td>0</td>
</tr>
<tr>
<td>Excessive REEs</td>
<td>0</td>
<td>0.968</td>
<td>8.7</td>
</tr>
</tbody>
</table>

As we can see from the leachate concentration columns divalent ions concentrations in the real leachate are 6 and 14 times higher than the synthetic ones for magnesium and calcium, respectively. The trivalent ions and silicon concentrations are similar. Looking at the six tested critical REEs concentration, it can be seen that they have different concentrations compared one to each other and to the synthetic leachate ones. The real leachate critical REEs average concentration, however, is 0.16 mg/L, close to the synthetic one. Considering also scandium as critical element, we can state that in real coal ash leachate the critical REEs are 43.5% of the total REEs amount. The pre-treatment removal efficiency for divalent ions and iron is similar for the synthetic and real leachates. Only almost 9% of the present aluminum is removed from the real leachate, compared to 50% in the synthetic one. The pre-treatment efficiency is enhanced in the case of silicon with a removal of 88.9% of the initial amount, more than twice the synthetic leachate efficiency. The pre-treatment removal for critical REEs is variable depending on the REE considered, even if their average efficiency (11.9%) is close to the synthetic one. The important thing to be noticed is the almost
90% loss of scandium in the pre-treatment step. This can be due to its adsorption on the major elements precipitates. Since scandium provides the majority of the economic return of the process, a deeper investigation on the pre-treatment effect on scandium should be performed. It is suggested to study the use of a base other than NaOH, to increase the pH to 4, trying to simultaneously remove divalent ions without losing scandium. The major elements rejection performed by the NF membrane is similar in the two cases, except for calcium whose rejection decreased of 15%. However, considering that less aluminum and more silicon have been rejected in the real leachate pre-treatment, we expect a higher and lower concentration in the NF retentate stream for aluminum and silicon, respectively. The real study REEs rejections are lower than in the synthetic leachate and they are different one to each other. The lower rejection could be due to the higher ions concentration in the NF feed that reduce the Donnan potential and thus the ions rejection. It is interesting to notice that for critical REEs, the higher the NF feed concentration the higher the NF rejection. In fact, Yttrium, that has the highest raw leachate concentration and lowest pre-treatment removal efficiency, resulting in the highest NF feed concentration, is the most rejected critical REE. On the other hand, Terbium, that has the lowest raw leachate concentration and highest pre-treatment removal efficiency, resulting in the lowest NF feed concentration, is the most rejected critical REE. Considering the sum of the six analysed critical REEs concentrations in the real NF feed and permeate an overall REEs rejection of 95.41% is achieved.

The high amount of rejected elements increases the cake formation and fouling of the NF membrane, resulting in a permeate flux decrease, from 17.3 LMH for the synthetic leachate to 11.6 LMH for the real one.

Since REEs in real leachate nanofiltration showed to be rejected differently, according to their NF feed concentration, more experiments should be carried out on the real leachate to understand the flux and rejection mechanisms when more elements are present in the solution at different concentration. The experimental data for real leachate should be considered to build new models for NF REEs rejection and NF permeate flux as function of elements concentration. The pre-treatment optimization outcome and NF performance models should then be used in a new economic model to study the feasibility of the process when real leachate is considered the feed of the membrane-based recovery step.
4.7. Analysis of membrane foulants

In order to understand the membrane fouling process during leachate nanofiltration, the membrane foulants after the operations were identified with basic weighing, SEM-EDS and XPS analysis. Every analysis for the fouling determination was carried out with 3 samples. The foulant amount per membrane area and the correspondent leachate permeability for each study are given in Figure 4.22.

![Figure 4.20](image-url) Foulant amounts per membrane area and leachate permeability at different pH and leachate conditions.

The foulant amount per membrane area changed in a range of 56.7-206.7 mg/m², regardless the filtrated leachate characteristics. It can be said that the pH and the type of feed leachate is significantly effective for NF membrane fouling. The minimum fouling was seen when pH was 1.5 during a synthetic leachate filtration. The reason for this minimum foulant amount is the observed minimum rejection for all element at that pH. When the rejection was low, the foulant amount on the membrane surface was also low as expected. In synthetic leachate NF tests, the amount of foulant doubled when pH increased from 1.5 to 3.5, reaching 126.7 mg/m². Real leachate filtration resulted in higher fouling, 206.7 mg/m², when compared to the fouling in the synthetic leachate filtration at pH 3.5, because of its more complex recipe and the higher amount of ions present in it. Looking at the NF membrane permeability, it can be said that it decreased with the increase in the amount of foulants on the membrane surface. While the maximum permeability was 0.72 LMH/bar, it decreased to 0.54 LMH/bar when
synthetic leachate pH increased. Using real leachate, permeability further decreased to 0.39 LMH/bar.

After the basic investigation of foulants, the SEM/EDS investigation was carried out for bare and fouled membranes. Figure 4.21 presents SEM images showing the formation of significant fouling on the membrane surface. SEM images confirmed the variation in the extent of fouling between the studies as observed by weighting and gave further ideas about the foulant structure. In order to identify the composition of the fouling layer, EDS analysis was conducted on the fouled membrane (right part of Figure 4.21).

a) Bare membrane

b) Fouled membrane sample from SL filtration at pH 1.5
c) Fouled membrane sample from SL filtration at pH 2.5

d) Fouled membrane sample from SL filtration at pH 3.5

e) Fouled membrane sample from RL filtration at pH 3.5

Figure 4.21. Comparison of SEM micrographs (left) and EDS analysis (right) of NF membrane samples from different leachate filtration studies (SL: Synthetic leachate, RL: Real leachate).
The bare membrane has a smooth and undamaged polymeric surface as expected. Although it is impossible to detect clearly the pores of an NF membrane via SEM, it can be said that this DK membrane has a homogenous pore distribution and there is no significant structural defect. According to the EDS analysis of bare membrane, it can be mentioned that there is only carbon, oxygen, sulfur and chlorine, which are directly related to the membrane raw materials. When the SEM images in Figure 4.21 for a used and a bare membrane are compared, it can be seen that the leachate filtration resulted in a fouling layer and it is not possible to see the surface of bare membrane although the foulant amount is low at that pH. The scaling increased with an increasing pH because of the high amount of rejected elements. Crystalline substances were identifiable. The clusters of hills created by rejected salts were bigger and more common on the fouled membrane surface used for the leachate filtration at pH 3.5.

After a real leachate filtration, the scaling and formation of hills were at maximum level. The inorganic fouling was obvious, and there were star and leaves shaped huge crystals on the membrane surface. Some of the foulant group had a size of 5 μm. These big crystals were covered with the free ions. The general type of the foulant in Figure 4.21 b-e can be described as solid and individual structures having sharp shapes and different sizes. The reason of this was dry samples and no presence of any organic foulants. Given that microfiltration filter had been used to pre-treat the leachate, the NF feed was likely to be free from larger size fly ash particles. However, finer particles might remain in the feed and subsequently form part of the fouling layer. The size of crystal clusters from the rejected salts resulted in a decrease in permeate flux. Flux decline was because of the pore blocking by the heterogeneous crystallization which can be described as a lateral growth of deposit on the membrane surface (Gilron and Hasson, 1987).

EDS analytical results are also given in Table 4.12. The presence of carbon and oxygen on the bare membrane surface and their absences for all the other samples are the main sign for an inorganic fouling. The high levels of Al and Si in the foulant layer suggest that it can be mainly aluminum silicates, however, it needed further analysis to be sure on the formed compounds at different pH values. It can be seen that REEs in the foulant could be determined when pH is higher than 1.5. While there was Yttrium in the foulant of membrane used for the synthetic leachate filtration at pH 2.5, Erbium added into the list of detected REEs when pH was 3.5. The reason for the higher possibility to determine more REE on the foulant layer is higher rejection with higher pH because the initial concentration of REEs is quite low when it is compared to the initial concentration of other major elements. It was obvious that the number of elements that
could be determined in the foulant layer of membrane used for the real leachate filtration was higher than in synthetic leachate tests. The complex structure of real leachate is the main cause of this result and scandium, lanthanum, cerium, and terbium could be detected.

**Table 4.12.** EDS analytical results for NF membrane surfaces.

<table>
<thead>
<tr>
<th>Element</th>
<th>Weight percent (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Bare M.</td>
</tr>
<tr>
<td>C</td>
<td>81.6</td>
</tr>
<tr>
<td>O</td>
<td>13.29</td>
</tr>
<tr>
<td>S</td>
<td>4.96</td>
</tr>
<tr>
<td>Cl</td>
<td>0.15</td>
</tr>
<tr>
<td>Na</td>
<td>-</td>
</tr>
<tr>
<td>Al</td>
<td>-</td>
</tr>
<tr>
<td>Si</td>
<td>-</td>
</tr>
<tr>
<td>Ca</td>
<td>-</td>
</tr>
<tr>
<td>Fe</td>
<td>-</td>
</tr>
<tr>
<td>Y</td>
<td>-</td>
</tr>
<tr>
<td>Nd</td>
<td>-</td>
</tr>
<tr>
<td>Eu</td>
<td>-</td>
</tr>
<tr>
<td>Tb</td>
<td>-</td>
</tr>
<tr>
<td>Dy</td>
<td>-</td>
</tr>
<tr>
<td>Er</td>
<td>-</td>
</tr>
<tr>
<td>Sc</td>
<td>-</td>
</tr>
<tr>
<td>La</td>
<td>-</td>
</tr>
<tr>
<td>Ce</td>
<td>-</td>
</tr>
<tr>
<td>Tm</td>
<td>-</td>
</tr>
<tr>
<td>Total</td>
<td>100</td>
</tr>
</tbody>
</table>

*M: Membrane, SL: Synthetic leachate, RL: Real leachate*

EDS was helpful to have important ideas on the elemental composition of the foulant layers and their changes with the change of pH and feed characteristics, but it was not enough to decide the type of the metal compound and their oxidation level. Within this regard, XPS analyses were carried out. Figure 4.22 presents XPS results quantifying the surface elemental composition of the unfoiled and fouled DK membranes.
The XPS results show that the active layer of DK membrane contained carbon, oxygen, and nitrogen and their ratio \((\text{C}:\text{O}:\text{N})\) for the bare membrane was 79.8:12.3:5.3. Compared to the unfouled bare membrane, all fouled membranes contained a lower proportion of carbon but a higher proportion of oxygen. The increase in the amount of oxygen can be related to inorganic precipitates which can contain oxygen via hydroxides and oxides. Inorganics in the foulant layers included sodium, silicon, aluminum, scandium, and yttrium. Sulphur was found on the surface of unfouled bare membrane and used membrane for the synthetic leachate filtration under pH 1.5 conditions. It may be said that the source of sulphur can be the sulphone-based support layer of the commercial thin film nanofiltration membranes. Membranes could be
damaged before the XPS analysis and the sulphur in this support layer could be analyzed for these membranes, because it cannot be mentioned that there is real sulphur foulant layers for these membranes. Calcium and chlorine that was determined on the surface of bare membrane may indicate the residue of a possible protective coating or a leakage from the support textile to the membrane surface since the XPS analysis of bare membrane was carried out without a compaction with NP water to get rid of any contamination before the analysis.

For all synthetic leachate studies, the amounts of sodium, silicon and aluminum in the foulant layers are higher at pH 3.5 when compared to their amounts at pH 1.5 as expected. The rejection of cations was higher with higher pH values and higher pH resulted in higher inorganic precipitation on the membrane surface. In the survey of the foulant layer obtained from the membrane used for the synthetic leachate filtration, the binding energy peak for silicon was found at 102 eV, suggesting that silicon was present as silicate (SiO₄). In the survey of the foulant layer obtained from the membrane used for the real leachate filtration, the binding energy peak for silicon was found at 102.6/102.7 eV, suggesting that silicon was in the form of aluminosilicate.

The XPS results therefore indicated that:

(i) sodium, silicon and aluminum fouling was more abundant for synthetic leachate when pH was between 1.5 and 3.5;
(ii) in both synthetic and real leachate studies, silicon was not present as free metal ion.

In synthetic and real leachate filtration, the silicon compounds formed in the rejected layer were silicate and aluminosilicate, respectively.

(iii) it was hard to determine the presence of rare earth elements due to their lower concentrations in the NF feed compared to major elements;
(iv) only Yttrium could be seen with a very low concentration in the foulant of membranes used for high pH studies.
4.8. Bibliography


Chapter 5 - Conclusions and future developments

Before considering coal fly ash as REEs alternative source, a comprehensive analysis of the efficiency and feasibility of REEs recovery processes is necessary. In particular, the main goal of this study consisted in optimizing the processes design to guarantee an economically feasible REEs recovery. At this scope, modeling REEs recovery performance and feasibility of REE-enriched acid leachate nanofiltration, as function of operating design parameters, is essential.

This study has demonstrated that pH adjustment and microfiltration are useful NF pre-treatments separating major elements precipitates and enhancing REEs purity. Furthermore, NF membrane, applied pressure and NF feed pH have shown significant effects on nanofiltration permeate flux and REEs rejection. In particular, PES membranes (NP010, NP030) have demonstrated REEs rejection lower than 15%, regardless the operating conditions. Thin film DK membrane has been selected has the optimal membrane because of its higher permeate flux and REEs rejection compared to the thin film Duracid membrane.

NF feed pH showed a positive linear effect on REEs rejection, due to the higher ionic concentration at lower pH resulting in Donnan potential reduction and ions permeation. Higher REEs and major elements rejection at increasing pH resulted in higher membrane fouling and lower permeate flux. Permeate flux showed a linear increase with the applied pressure, in accordance to Spiegler and Kedem theory. Response Surface Methodology allowed the detection of the interaction effect between applied pressure and NF feed pH on both REEs rejection and permeate flux.

The economic model describing the REEs recovery line proved that, considering the performance models developed on synthetic leachate experimental data, the designed process is economically feasible. The major cost contribution is due to the NF step, while the main return results from scandium sale. The specific gain per kg of treated coal fly ash increased with the NF feed pH leading to choose the optimal pH as 3.5. At this pH, pressure showed no significant influence on the specific gain. The minimum analyzed pressure, 12 bar, has been selected as the optimum for safety and equipment maintenance reasons.

The test conducted with the optimized processes on a real leachate sample demonstrated lower permeate flux and REEs rejection than the synthetic leachate test. This has been explained with the higher ions concentration in the real leachate, resulting in both membrane fouling, decreasing the permeate flux, and Donnan potential reduction, increasing ions permeation. In particular, REEs in real leachate
nanofiltration showed to be rejected differently, according to their NF feed concentration.

This research has proved evidences of the influence of membrane, applied pressure and NF feed pH on synthetic leachate NF performance. These findings will need to be validated with real leachate to identify possible unexpected trends compared to the synthetic leachate tests results. The only performed real leachate test highlighted the need to further investigate the effect of major elements and REEs concentration on NF performance. NF performance models should be developed considering main and interaction effects of applied pressure, NF feed pH and ions concentrations. In fact, should this be possible, the NF permeate flux, REEs rejection and specific gain could be precisely predicted based on the operating conditions and leachate concentrations and, consequently, the REEs recovery process could be optimized and tailored specifically to the type of coal fly ash.