Final report: Critical metals hidden in ash – filtration and extraction of magnesium from solutions of oil shale ash (22-145)

Summary

In this academic-industrial research project a number of porous organic polymeric materials have been synthesized with the aim to develop sieving materials targeting the extraction of magnesium ions from dissolved oil shale ash (OSA). OSA is an inorganic industrial waste material deposited in enormous quantities across northern Estonia, close to the Gulf of Finland. Different ordered and disordered organic polymers containing a range of chemical functionalities have been developed and tested to determine metal-ion adsorption capability and selectivity. Similarly, we have investigated different routes to solubilize OSA and release the “hidden” metals inside by leaching with different acids. The main conclusion from these studies is that while tailored covalent organic frameworks have the potential for very efficient metal ion adsorption capability, however, the route for regenerating the metal ion collectors and simultaneously release the ions needs further studies.

Background

Oil shale ash (OSA) is the collective term for the ash that remains after burning of oil shale. Oil shale is a type of rock with large solid organic content and the organic material can be directly burned in power plants or processed to give liquid hydrocarbons (oil). In Estonia, this process has been ongoing for over a century and has generated huge quantities, hundreds of millions of tonnes, of OSA which are deposited in heaps across northern Estonia. Oil shale ash contains large quantities of alkaline calcium oxide, metal oxides - primarily magnesium, iron and aluminium, silica, and small amounts rare earth metals and remaining organic matter. Our industrial partner and its subsidiaries together with the primary ash owner are now aiming to establish processes that can extract more of the materials hidden in the ash to kick start a green and circular industrial revolution in the Baltics. Processes to valorise the waste and extract calcium carbonate is in pilot plant and the next target is magnesium. Analysis by the waste owner indicates thousands of tons of magnesium are present in the deposited OSA, enough to supply Europe for many decades, which awaits a method to realize it.

Magnesium is used across a range of industries and is classified as a critical raw material by the European Union. This classification comes from both its importance for European industry in combination with limited suppliers. An estimated 93% of the magnesium used today is imported from one country, China. The fear is that a geopolitical crisis could almost completely cut European magnesium import.

In this academic-industrial research project we have (and continues to) explored routes to selectively capture magnesium ions to allow for valorisation of the oil shale ash. We have also applied our methodology on other types of inorganic industrial residues with the aim to contribute to the ongoing research to develop more sustainable forms of mining. The aim for this line of research is to allow a higher percentage of the valuable metals present in excavated soil and rock to be utilized in order to minimize environmental impact.

Results and methods

The work has been divided into different work packages (WPs) and during the first year of the project the focus has been on WP1 and WP2 targeting design and synthesis. In year two the focus shifted more towards studying release and regeneration of the materials (WP3) and also to test the materials towards relevant metal ion mixtures.

In WP1 the composition of the ash and how it behaves at different pH have been systematically investigated. The aim of the process is to dissolve the ash and the metal oxides into a water solution. This solution can then be pumped through, or over, a “capture” material which binds the desired ion with high selectivity. OSA is a complex material containing many different elements which have different solubility at different pH. Thus, to simplify the separation process it would be beneficial to maximize solubility of e.g., magnesium (the target in these studies) and minimize everything else. Metal oxides are generally dissolved in acidic conditions and the primary focus has been on acidic pH. Together we have explored a range of different mineral and organic acids e.g., sulfuric acid, hydrochloric acid and different organic acids. Employing inductively coupled plasma (ICP) studies on the different aqueous OSA solutions reveal that organic acids preforms surprisingly well and there exists pH ranges at moderate pH where dissolution of magnesium is favoured compared to other metal oxides. These results form the basis for the design of sieving materials in WP2. In a future industrial process, the environmental impact, cost and (re)usability of the acid would need to be evaluated more carefully in relation to how efficient the dissolution process is. This is beyond the scope of this study.

What is clear from WP1 is that the materials used need to withstand acidic conditions, especially considering that release of ions coordinated to organic functional groups traditionally employs strong acids to protonate the functional groups and thus expel metal-ions. This has implications for future studies to release the trapped ions (WP3). With this in mind a range of polymeric material has been designed, synthesized and investigated in our labs as part of WP2. These studies have continued during the entire project with material being evaluated, the designed tweaked and the new improved material tested again. WP4 includes the testing of authentic oil shale ash solutions and was due to time constraints mostly beyond the scope of the project. However, these studies are continuing as part of our ongoing academic-industrial collaboration and will be reported in due course.

Thus, the primary purpose of the research was to evaluate porous organic frameworks as sieving/ion-exchange extractor materials. However, we also desired to compare these ordered materials performances versus discorded porous polymers. In addition, while there are certain chemical structures known in the literature to coordinate strongly to magnesium, we also desired to investigate a larger chemical space and explore the combination of ordered/disordered polymers, pore size and chemical functionality. Figure 1 shows examples of these considerations and structures.

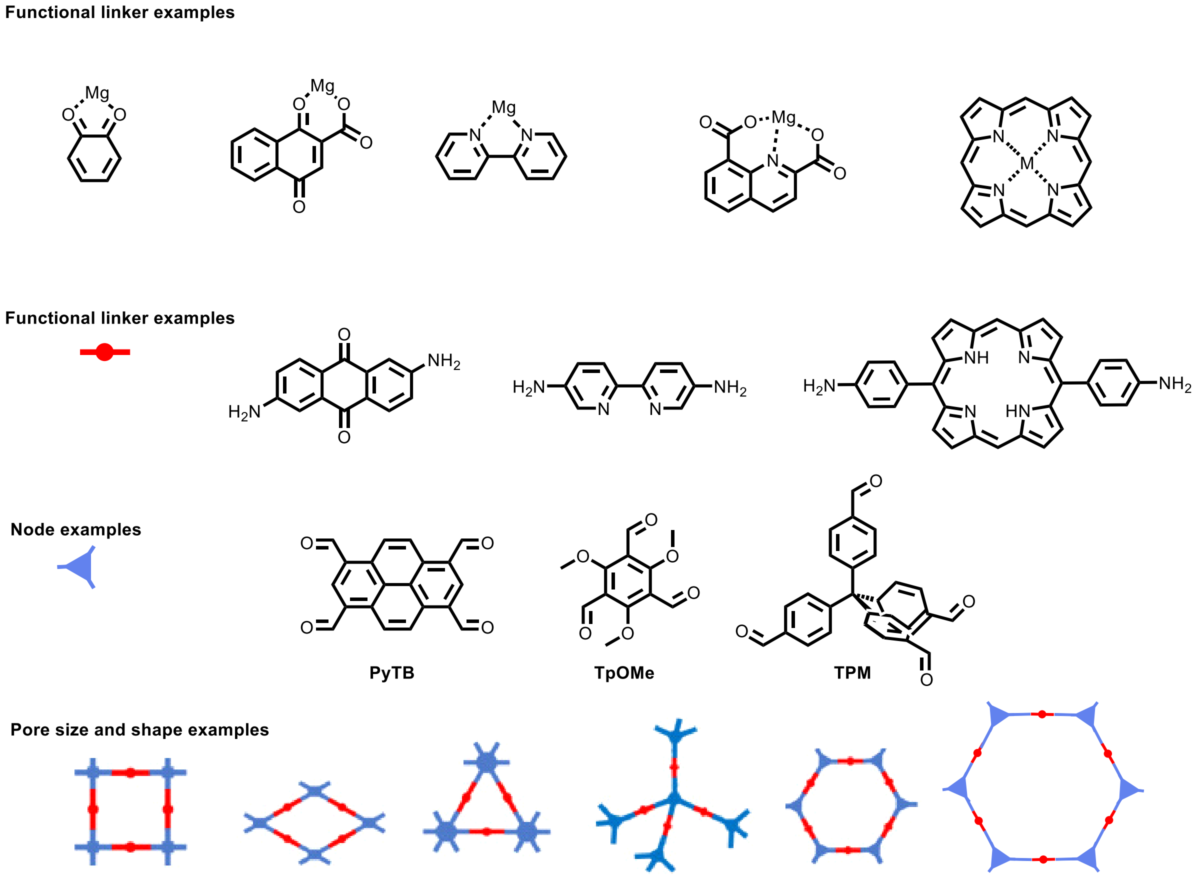

Figure 1. A general summary of the strategies and materials employed in the studies showing different chemical structures and how these interact with metal ions (in this case magnesium ions). Below follow some examples of these functionalities incorporated in a chemical linker structure suitable for polymer formation and the corresponding nodes used to assemble the porous polymer. Examples of how different nodes affect pore size and shape are given at the bottom with linkers (red) and nodes (blue). The aim is to combine different chemical functionalities in different polymers to utilize both that metal ions binds to functional groups and that the ions are different in size to achieve selectivity.

In practice we have synthesized a number of organic frameworks based primarily on 1,3,5-trimethoxy-2,4,6-carbaldehyde benzene (**TpOMe**) but are also studying for example pyrene derivative (**PyTB**) and tetraphenylmethane (**TPM**) as the node among others. In particular **TpOMe** is interesting as we and others have previously explored it in other applications where the resulting organic frameworks are stable for several days even in concentrated sulfuric acid, e.g. in extremely corrosive environments, The resulting polymer is formed by an acid promoted condensation between the aldehyde groups of the node and an appropriate functionalized diamino building block employed as the linker. A mechanochemical approach (grinding with a ball mill or pestle and mortar) followed by heating (ranging 50-120°C) yields the desired polymer after 12-36 h. Importantly, the synthesis is scalable and could theoretically be used industrially, however, this need to be explored further in future studies. The resulting polymeric materials are then sequentially washed with a range of solvents (DMF, water, ethanol etc) to remove any remaining unreacted building blocks, acid and/or solvents. Materials properties of the synthesized material vary depending on the choice of linker and node. Apparent BET surface areas (a measure of how porous the material is in square meters/gram, not necessarily translatable into the same number on the macroscopic scale) show porosities ranging from 500 m^2/g up to over 3000 m^2/g. Figure 2 shows examples of structure of such frameworks based on **TpOMe** using different functionalized linker.

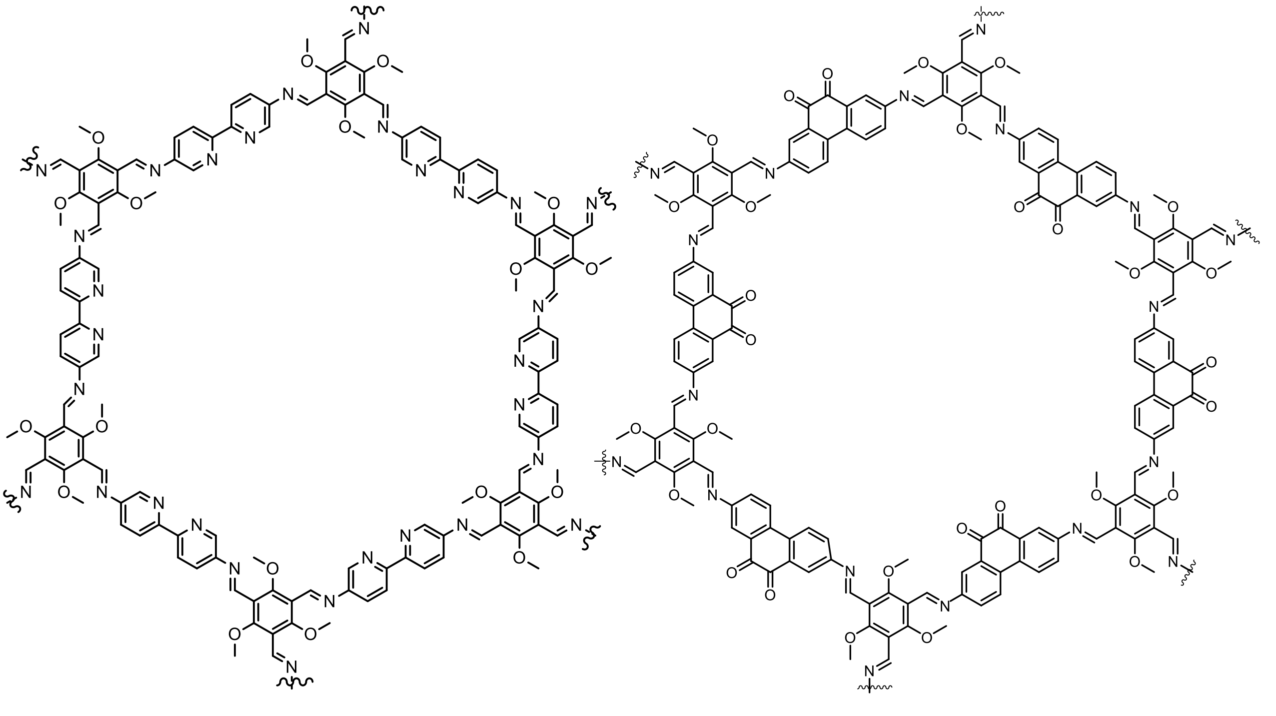

Figure 2. The chemical structure of two different organic frameworks synthesized in this project. Both employs the **TpOMe** node while varying the functional linker.

Similarly, we have devised and carried out synthesis of polymers intended to be porous, but unlike organic frameworks, not crystalline. E.g., these materials did not show the same degree of long-range order as the frameworks. Variants of the node possessing only some of the functionalities at different positions, or a modified synthetic protocol with more solvent present during synthesis, results in amorphous materials with acceptable porosity (ranging 50-800 m^2/g). The materials characterization of these material shows limited long-range order using powder x-ray analysis confirming the amorphous, yet, porous structure.

Both the ordered and disordered materials have been screened using aqueous laboratory stock solutions of dissolved magnesium ions to first determine adsorption capability and different pH using the acids and results from WP1. A range of concentrations have been used and the results are currently being summarized in two separate manuscripts detailing these results and providing a structure-property relationship to guide further studies. These will be published once any potential patent applications have been resolved. The results clearly indicate that some combinations of solution composition and material characteristics have both very high adsorption capability as well as excellent selectivity towards targeted ions in semi-complex (containing one additional ion type) and complex (containing several ions) laboratory solutions. It should be noted that the effect of the acid is pronounced as even the best performing materials have mediocre selectivity in some acid solutions. This effect is likely due to coordination or ion-paring of these ions which modify the atomic radius and thus tuning their size and electronic structure.

Studies are underway to optimize the conditions for high selectivity and capability and expand on the structure-property relationship. For magnesium extraction from OSA residual calcium and iron, the two main components of OSA, are crucial to address. The above laboratory solutions show promising results and studies using authentic OSA solutions are currently underway to determine capacity and selectivity also for these (work towards WP4).

The main challenge which still needs to be addressed concerns the release of trapped ions and the regeneration of the material (focus of WP3). Here, more work is needed to ensure complete expulsion of the trapped ions. The idea is for the polymeric material to be stationary and long-lasting allow continuous or batch extraction from water solutions. Thus, it is crucial the release and regeneration are highly efficient and that adsorption capability of the polymeric extractors remain high after consecutive trappings/releases. Currently the drop in capability is too high in relation to the effort needed to synthesize the material and further studies are needed to improve these metrics.

Future studies

The project has yielded very promising results and we are currently planning follow up studies together and new joint research applications together. Focus for these will focus on efficient release of trapped ions and maintained capability of the polymeric extractor material. The same materials will also be screened for other types of processed inorganic waste to explore wider applications.