Institution:
University of Lincoln

Unit of Assessment:
08 - Chemistry

Title of case study:
Recovery and Recycling of Rare Metals

Period when the underpinning research was undertaken:
2009 to date

Details of staff conducting the underpinning research from the submitting unit:

Name(s):	Role(s) (e.g. job title):	Period(s) employed by submitting HEI:
GONZALEZ-RODRIGUEZ Jose	Associate Professor/ Programme Leader	2 May 06 to date
BARON Mark	Associate Professor	1 Sep 00 to date

Period when the claimed impact occurred:
2015 to date

Is this case study continued from a case study submitted in 2014?
N

1. Summary of the impact (indicative maximum 100 words)

Several rare metals important in the production of super alloys and components for a range of industrial sectors are particularly scarce, difficult to mine or recycle. Due to their complex chemistry, traditional methods do not offer a full solution for their extraction and recycling. In response, research at the University of Lincoln has developed innovative extraction methodologies, leading to improved industrial processes in the field of rare metal extraction from petroleum ash. By **improving process technology** for GSA environmental Ltd (GSAe), this has **enhanced GSAe's commercial portfolio and overseas investment.** In turn, GSAe have been able to implement these novel processes with international partners resulting in **economic benefits for the Venezuelan State Oil Company,** alongside increased purity and extraction yield.

2. Underpinning research (indicative maximum 500 words)

The aviation, energy and digital technology industries are reliant on specific rare metals such rhenium, vanadium and yttrium to produce super alloys and key components. However, these elements are not only scarce but also difficult to mine and costly, slow and inefficient to recycle. Without these elements, these industries are unable to produce the key materials necessary for their sustainability, necessitating innovative solutions to maximise extraction.

Dr Jose Gonzalez-Rodriguez and Dr Mark Baron at the University of Lincoln have led a series of research studies to examine rare metal extraction and develop more efficient and effective approaches. The team first examined traditional approaches using precipitation and distillation methods for extraction of rhenium, an element that is added to high-temperature superalloys that are used to make jet engine parts and blades for power generators. Initial research led to the development of a quick and simple technique for the analysis of rhenium in powder samples using infrared spectroscopy **[Reference 3.1].** Supported by both a Higher Education & Regional Fellowship (2010) and follow-on support from the University of Lincoln Dr Gonzalez-Rodriguez and his team carried these developments into next stage research to explore alternative approaches to traditional hydrometallurgical extraction. By processing polymers with a molecular imprinting technique (MIP) that leaves cavities in the polymer matrix with an affinity for a chosen "template" molecule, rare metals (as defined by the template) become attached to the polymers. The research team not only tested this new approach for rhenium but also developed a specific method to design and produce a polymer for the extraction of rhenium from scrapped super alloy material, enabling further development of new polymer technology. This research led to the development of a holistic and novel methodology for both the dissolution and manufacturing of rhenium-selective MIPs, as well as an economic assessment of the technology. **[References 3.2 and 3.3]**

In 2013, the team established an Innovate UK Knowledge Transfer Partnership (KTP) with a national engineering company, GSA environmental Ltd (GSAe). This collaborative research programme established methods to selectively extract vanadium, nickel and molybdenum from ashes obtained in the fuel-oil burning process to obtain energy in power plants. A key project aim was the recovery of other metals present in the ash residue to identify opportunities for recycling and commercialisation of the carbonaceous matrix left after the extraction. Dr Gonzalez-Rodriguez and colleagues evaluated the extraction yield and purity of the metals obtained via different methodologies (eg solvent extraction, Ionic liquids, ion exchange, precipitation). The team optimised variables associated with the leaching solution used to extract metals from the ashes (pH, ionic content, oxido-reduction potential) to deliver novel processes which achieved superior results to traditional methods. This research also enabled the team to develop new methods of analysis of solid ash samples using atomic absorption spectroscopy **[Reference 3.4].** The practical application of MIPs was tested in the final phase of this project in order to explore their potential for the extraction of these metals, successfully achieving some initial polymers selective for these metals.

A second Innovate UK KTP with GSAe Ltd was awarded in 2017 to further develop the use of MIPs for the selective extraction of vanadium from ashes, building on the team's earlier work extracting rhenium using this method. Using a process patented by UoL in 2014 **[Patent listed as reference 3.5]**], the research conducted as part of this KTP led to the development, test and manufacture of a polymer 100% selective for vanadium **[Reference 3.6].**

These highly novel research findings confirmed polymer technology as one of the most promising alternative approaches to recycle and recover rare metals from materials including rare earth and scrapped digital technology components.

3. References to the research (indicative maximum of six references)

3.1 Gonzalez-Rodriguez, J., Pepper, K., Baron, M.G., Mamo, S.K. and Simons, A.M., 2018. Production and Analysis of Recycled Ammonium Perrhenate from CMSX-4 superalloys. *Open Chemistry*, *16*(1), pp.1298-1306. https://doi.org/10.1515/chem-2018-0136 https://www.degruyter.com/view/journals/chem/16/1/article-p1298.xml?language=en

3.2 Mamo, S.K., Elie, M., Baron, M.G., Simons, A.M. and Gonzalez-Rodriguez, J., 2019. Leaching kinetics, separation, and recovery of rhenium and component metals from CMSX-4 superalloys using hydrometallurgical processes. Separation and Purification Technology, 212, pp.150-160., Separation and Purification Technology (2019). https://doi.org/10.1016/j.seppur.2018.11.023

3.3 S. Mamo, M. Elie, M. Baron, J. Gonzalez-Rodriguez* (2020). Computationally designed perrhenate ion imprinted polymers for selective trapping of rhenium ions. ACS Applied Polymer Materials. Accepted. https://doi.org/10.1021/acsapm.0c00337

3.4 Valdivia, A.C., Alonso, E.V., Guerrero, M.L., Gonzalez-Rodriguez, J., Pavón, J.C. and de Torres, A.G., 2018. Simultaneous determination of V, Ni and Fe in fuel fly ash using solid sampling high resolution continuum source graphite furnace atomic absorption spectrometry. Talanta, 179, pp.1-8. Talanta 2018 https://doi.org/10.1016/j.talanta.2017.10.033 https://www.sciencedirect.com/science/article/pii/S0039914017310706?via%3Dihub

3.5 Application number PCT/GB2014/051390. Publication number WO2014188158 METALS RECOVERY METHOD AND POLYMER FOR USE IN METALS RE-COVERY AND PROCESS FOR MAKING SUCH A POLYMER (2014).

(https://patentscope.wipo.int/search/en/detail.jsf?docId=WO2014188158&recNum=1&maxRec=&office=&prevFilter=&sortOption=&queryString=&tab=PCT+Biblio)

3.6 Partners Final Report to Innovate UK (KTP KTP010899), University of Lincoln and GSA Environmental, with Assessment, September 2020. Available on request.

4. Details of the impact (indicative maximum 750 words)

Through a successful industrial partnership with GSA-e, research carried out in the University of Lincoln School of Chemistry has led to improved industrial processes in the field of rare metal extraction from petroleum ash. By **improving process technology for GSAe** via new technical protocols for enhanced metal extraction, this has **enhanced GSAe's commercial portfolio and overseas investment.** In turn, GSAe have been able to implement these novel processes with international partners resulting in **economic benefits for the Venezuelan State Oil Company,** alongside increased purity and extraction yield

Improving process technology for GSAe

As part of the initial KTP with GSAe, the company worked with Lincoln researchers to test and optimize the company's process technology for the extraction of vanadium, nickel and molybdenum from industrial waste. The collaborative work revealed that the company's existing processes were sub-optimal, and further work was carried out to develop new process technologies. As a result of Lincoln's research activities, GSAe report having been able to increase their knowledge of the environmental impact related to their source process material, increase their targeted client base, offer a more hybrid solution to an increased number of clients with lower concentration of metals contamination, and reduce their operational energy and water usage by up to 50% **[5.1].** The new processes have been described by GSAe as 'paramount' in enabling them to deliver a project for Petroleum de Venezuela SA (PDVSA), the Venezuelan State Oil Company, focused on optimising PDVSA's processes**. [5.2]**

Enhancing GSAe's commercial portfolio and overseas investment

As well as the project with PDVSA, by incorporating UoL-led research into their process technology, GSAe's have been able to further develop their commercial portfolio and extend their business activities in metal extraction. These increased business activities have led to significant overseas investment, with GSAe stating:

> *Our relationship with the University of Lincoln has been very valuable, with their research in metal extraction enabling us to extend our business activities sufficiently to attract investors … to acquire a substantial part of the company. This has had a great impact for us, not only in terms of financial stability, but also in the business opportunities overseas … and global visibility".* **[5.2]**

The Vanadium specific polymer developed as part of the second KTP collaboration [see 3.6] with GSAe is capable of recovering vanadium with sufficient purity (>99%) to be utilised as an electrolyte for the new generation of V_2O_5 rechargeable batteries. These batteries are a key component of new technology for the storage of energy from renewable sources. This has already opened a series of new commercial options for GSAe who report:

> *"The technology transfer from the University to manufacture this polymer has had a positive impact in enhancing [GSAE's] portfolio. The research has facilitated the company to access new state-of-the-art technology in the manufacturing of selective polymers. This novel technology will help reducing extraction costs, proving more efficient in the recovery of valuable metals as compared to existing alternative methods. At the moment the company is considering patenting and evaluating its industrial and economic potential in the case of vanadium. This technology will be used and adapted to extract other valuable metals, such as scandium also in collaboration with the University of Lincoln"* **[5.2]**

Enabling economic benefits for the Venezuelan State Oil Company

Subsequent to collaboration with UoL, GSAe undertook a project for Petroleum de Venezuela SA (PDVSA), citing that *"The results obtained from this first KTP allowed GSAe Ltd to optimize PedeVeSA's industrial process"* **[5.2]**. This work focused on the extraction of vanadium, molybdenum and nickel from ashes produced from burning of crude oil, leading to significant financial benefits for PDVSA. By implementing the process technology developed as part of the KTP, PDVSA has reported a capital cost reduction of 30%, valued at USD10 million. These methods have increased vanadium recovery from <45% to >90% (valued at USD5 million USD per annum per project) and increased nickel purity from 60% to >90%, equivalent to a doubling in value (USD4 million per annum per project). Water consumption has also been reduced by up to 60%, enabling more projects to go ahead and benefitting the environment. More realistic mass balance and cost estimation models have also been created, reducing previous misestimates of operating costs by up to five times**. [5.2]**

5. Sources to corroborate the impact (indicative maximum of 10 references)

5.1 KTP 1 report and Innovate UK review.

5.2 Testimonial letter from GSAe.