



Figure 1. Jarosite and phosphogypsum heap.

# Waste heaps may be set to reveal their content of critical metals

PERTTI KOUKKARI, MARI LUNDSTRÖM, ANTTI PORVALI, SERGEI KIRILLOV

In the production of fertilisers and commodity metals large amounts of stabilised waste is generated. Conventionally, manufacturing is targeted at the recovery of economically and technically most attractive key elements while the inorganic waste stream will gather all the other added-value chemical quantities. For example, substantial amounts of rare earth metals, which are increasingly used in various modern technologies including cleantech and photonics are present in *phosphogypsum*, the voluminous waste of the worldwide fertiliser industry. There

are also other underutilized rare earth metal rich waste streams such as *NiMH battery* and *permanent magnet waste*. The *jarosite* waste of bulk zinc production includes, e.g. silver and typically critical metals such as indium and gallium, which have become of increasing importance for new energy, electronics and touchpad applications.

The waste heaps, while generally stabilised against weathering, appear usually granular or even as powder-like fines. Thus they represent a readily comminuted raw material for innovative mechanical, hydrometallurgical, biohydrometallurgical and

pyrometallurgical techniques to recover considerable amounts of valuable metals and metal concentrates.

## Content of critical metals and rare earths in waste piles and NiMH battery waste

Jarosite [typically of formula  $MFe_3(SO_4)_2(OH)_6$ , where M represents a metal cation (Na, K, Pb/2 etc.) or ammonium] is an industrially produced iron sulphate residue from bulk metal processing. Its most abundant source is electrolytic zinc production, which extends to 11–12 Mt/yr, >

the respective jarosite amount being up to 5 Mt/yr worldwide. Jarosite is typically compiled in the plant vicinity and within EU considered as hazardous waste. While zinc ore typically is a carrier of many other metals, the content of both base, valuable and critical metals in such heaps is significant. The analysis of typical jarosite stack shows content of zinc 2 %, lead up to 3%, and variable amounts (10-150 g/t) of valuable metals such as silver, indium and gallium. Iron content is at least 15 %. Such compositions are comparable with present day commercial ores.

Phosphogypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ; PG) heaps exist in over 50 countries, the annual stockpiling exceeding 200 Mt worldwide (exact figures are difficult to gain as, e.g., statistics in large Asian countries are not available). Russia has compiled 250 Mt and every year produces 4 Mt, in Finland the PG stacks exceed 50 Mt altogether with 1.5 Mt annual increase.

In the fertilizer manufacturing process even 80% of the REE will end up in the phosphogypsum side product, which then holds from 0.2 to 0.4 w-% REE. Thus the content of REE in each PG stack may vary. In Russia, the average is given as 0.4 % while in Finland the content is lower (0.17 %) due to the igneous phosphate rock used in the fertiliser process. Recovery of the REE from such piles yet would allow a considerable production volume reaching to 10–15 000 t/yr of REE.

Currently, in NiMH batteries, the most common anode electrode material consists of a hydride forming metal alloy of type AB<sub>5</sub>, containing light rare earth elements such as La, Ce, Pr and Nd. The content of REE in NiMH battery waste depends on the preprocessing of the fraction. According to Larsson (2014), one battery cell in portable 1kg battery contains approximately 13 wt% of REEs.

### Reprocessing jarosite for its metal values

Jarosite is the iron containing sulphate residue from many metallurgical industries. In largest amounts it is formed in electrolytic zinc production as a neutralisation product (sodium and ammonium jarosite). When typical zinc ores are being used as raw materials, the waste will include significant amounts of lead and silver in addition to residual zinc (due to this fact, some modern zinc facilities are converting their production lines for the recovery of silver as a side product).

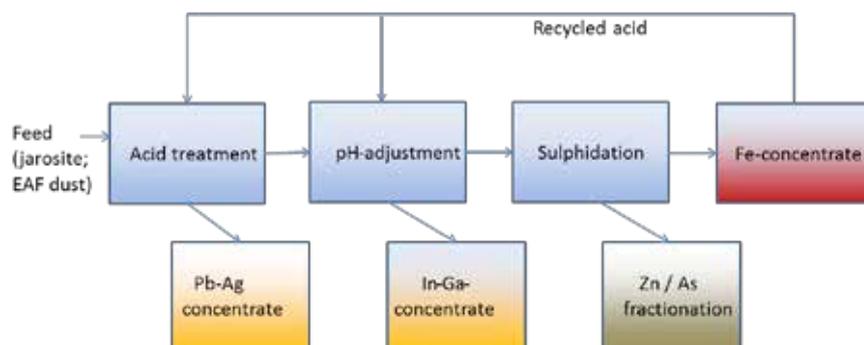


Figure 2. Block diagram of the Jarogain –process recovering value-added concentrates from jarosite waste.

The precipitation of jarosite will equally bind the minority metals present in the aqueous electrolyte solution into the M position. Thus, e.g., gallium is readily precipitated in jarosite-type compounds and the extent of gallium bound in jarosite increases as the Ga concentration of the solution increases. Similar precipitation behaviour is encountered with indium and thus these two critical metals are also often present in significant amounts in jarosite heaps.

Major research for utilising jarosite so far has been focusing on its uses as stabilised construction or landfilling component. Yet, as the stack necessarily contains but heavy metals also poisonous constituents (As, Cd), such developments have had limited success. Thus, it is conceivable that interest in reprocessing jarosite to recycled value added products has also been increasing during the last few years.

### Hydrometallurgical fractionation of jarosite

The hydrometallurgical fractionation process proposed by VTT and Aalto University in co-operation with experienced zinc process wizards (FI20165972) takes advantage of jarosite being readily powderous and directly available for hydrometallurgical processing. In a sequential holistic operation including controlled dissolution-precipitation steps four metal rich concentrates will be recovered. In the first stage the dissolution of the soluble constituents to sulfuric acid-sulfur dioxide leachant will allow subsequent precipitation of lead and silver as sulphides together with insoluble fines, from which Pb and Ag are recovered with conventional flotation techniques. Further pH adjustment of the overflow of the first stage will allow the recovery of In

and Ga rich hydroxide precipitate. Then, after pH- adjustment, Zn and As can again be recovered as sulphides. The process will be operated at non-oxidative conditions to maintain  $\text{Fe}^{2+}$  in soluble form until it will be deposited in an evaporation-crystallisation stage to ferrous sulphate. The precipitate will include Mg used in the former stages as the key neutralising agent. A roasting process will then be used to recover iron as hematite and to recycle sulphur dioxide. With further processing, MgO could be recovered via dissolution and with a secondary roasting stage. The originally insoluble sludge, from which Pb and Ag are removed does not contain harmful constituents and can be utilised either as a construction material or as landfill. Sulfur is recovered from the thermal treatment of sulphates and can be re-used in the first stage of the process or re-directed to zinc electrolysis. Finally the proposed process may be merged with treatment of zinc containing dust, typically originating from electric arc furnaces of steel plants. In such case, the amount of zinc and iron recovered will substantially increase, improving the process economy.

Potential production volumes of the bulk metals for the holistic Jarogain plant are presented in Table 2. The values are estimated for a plant processing 400 kt of jarosite material annually. Respective recovery of Ag, In and Ga concentrates could reach 5-60 t/yr, depending on source and process conditions.

The prices of metal products and concentrates are prone to large cyclic variations depending on the world economy, yet all the product metals are either those with established commodity markets (Zn, Pb, Fe) or those of increasing interest in many high-tech areas. In particular silver and

indium are known as indispensable for, e.g., novel solar energy techniques and touch screen electronics. Indium and gallium both belong to the metal and mineral products which are listed according to their critical availability within the EU region.

### Recovery of REE from phosphogypsum with solid ion exchanging adsorbent

Rare earth elements (REE) are as well classified as EU critical metals. The Finnish apatite minerals, industrially utilized for manufacturing phosphate fertilizers represent a potential secondary source of REE. In the current fertilizer manufacturing process even 80% of the REE will end up in the phosphogypsum (PG) side product, which then holds 0.15–0.5 % of REE.

So far economical means of recovering REE from apatite or PG have not been found. Novel active extraction or ion exchange methods as well as innovative biochemical methods have been recently examined by VTT and its co-operation partners.

In the conventional processing of Rare Earth Elements (REE) from dilute saline solutions containing large amounts of Fe, Al and other elements are typically formed. The extraction of REE then becomes an elaborate task to be solved by traditional hydrometallurgical methods. For example in the industrial scale the recovery of REE from these solutions is traditionally conducted via deposition by ammonia, alkalis and anions such as F<sup>-</sup>, S<sub>2</sub>O<sub>4</sub><sup>2-</sup>, and PO<sub>4</sub><sup>3-</sup>. Disadvantages of these methods include, e.g., a large loss of REE (20-25%) as coprecipitating hydroxides with metals such as Fe (III), Al, Zr and Ti. The waste waters caused by the large flow rates, chemicals used for precipitation and low regeneration rates can cause challenges.

Sorption and extraction are currently the most promising methods for extracting REEs from dilute solutions, since they have a high-performance and simple hardware design. They are also selective and well suitable for construction of closed circulation. Yet, even in such processes, the maximum extraction efficiency has appeared as a challenge (Yahorava & al. 2012). At Ural Federal University (Jekaterinburg, Russia) REE from phosphogypsum have been recovered by counter current acidic sorption leaching as described in figure 3. With the data received from the authors, a multicomponent process model has been developed at VTT (Co-op agreement RF-MEFI58114X0002, see Kirillov & al. 2016).

Component	Content	Annual production
Pb	3 %	12 000 t
Zn	2 %	8 000 t
Fe	15 %	60 000 t
Fe <sub>2</sub> O <sub>3</sub>		86 000 t

Table 1. Annual volumes of a holistic jarosite recovering plant.

Component	w-% in phosphogypsum (CaSO <sub>4</sub> ·2H <sub>2</sub> O)
CaO	32.5
SO <sub>3</sub>	44
P <sub>2</sub> O <sub>5</sub>	0.65
F	1.2
SiO <sub>2</sub>	0.5
Fe <sub>2</sub> O <sub>3</sub>	0.1
Al <sub>2</sub> O <sub>3</sub>	0.1
MgO	0.1
H <sub>2</sub> O (cryst.)	19
SREE	0.15-0.4

Table 2. Composition of phosphogypsum

	PG	SRB
La [ppm]	390	30 400
Ce [ppm]	1100	66 200
Y [ppm]	23	8 800

Table 3. REE enrichment from PG into the sulphate reducing bacteria (SRB) precipitate

With sulfuric acid leaching and commercial cationites as sorbents extraction efficiency of 60-65 % has been gained. The respective minipilot has been operated continuously to process a batch of 45 tonnes PG. The REE concentrate obtained was ca 100kg's with 48-54 % of rare earth elements.

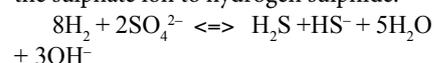
Desorption was carried out with a solution of ammonium sulphate. The choice of this reagent was dictated by the fact that further processing of the eluates will involve the use of ammonia and ammonium salts

to precipitate concentrates. Ammonium ions also have a good desorbing capability because of the affinity to cation binding functional groups in the adsorbent resin. To further refine the desorbed REE solution it was treated with 10% NH<sub>4</sub>OH. Pre-neutralization of the excess acidity with ammonia was necessary, firstly, to help reduce the formation of ammonium carbonate salts, and secondly, to precipitate bulk metal hydroxides such as Fe<sup>3+</sup>, Al<sup>3+</sup> simultaneously sorbed with REE. Precipitation led to pH 4.5-5. This interval is characterized by the end of the precipitation of hydroxides of the above metals.

Precipitation of REE as carbonates is a well-known process and can be performed by use of ammonium carbonate. With this treatment, a recovery rate of 75-80 % of REE as Ce<sub>2</sub>O<sub>3</sub> and light and heavy REM carbonate concentrates has been achieved with purity exceeding 99 % when up to 50 kg's of original REE concentrate solution has been treated.

### Passive treatment of PG with sulphate reducing bacteria

The use of sulphate reducing bacteria (SRB) for removing contaminants such as heavy metals from aqueous solutions is well known. The SRB can be used for treating ground- and surface waters contaminated with acid mine drainage (AMD), and for recovering metals from wastewater and process streams. The biologically produced H<sub>2</sub>S precipitates metals as metal sulfides, while biogenic bicarbonate alkalinity neutralizes acidic waters. In such method, the aqueous sulphate solution, provided with appropriate electron donor (either hydrogen or organic compound) is inoculated with micro-organisms, such as *Desulfovibrio* bacteria, which promote the reduction of the sulphate ion to hydrogen sulphide:



Instead of hydrogen, organic compounds descending form, e.g., fermentation processes or waste streams with anaerobic degradation stages and including, e.g., organic acids or alcohols can be used as electron donors. One may expect the SRB sulphide sludge to contain large fraction of the REM sulphides as a finely dispersed precipitate. The SRB sludge containing the insoluble REM (sulphides) will have high magnetic susceptibility and could be recovered from the bio-sludge by physical separation with a recently patented concept (FI 125550 B).

Preliminary results achieved by aqueous >

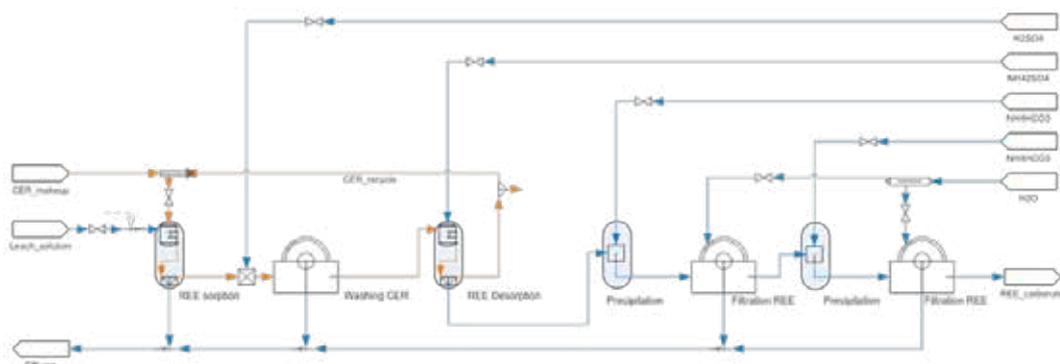
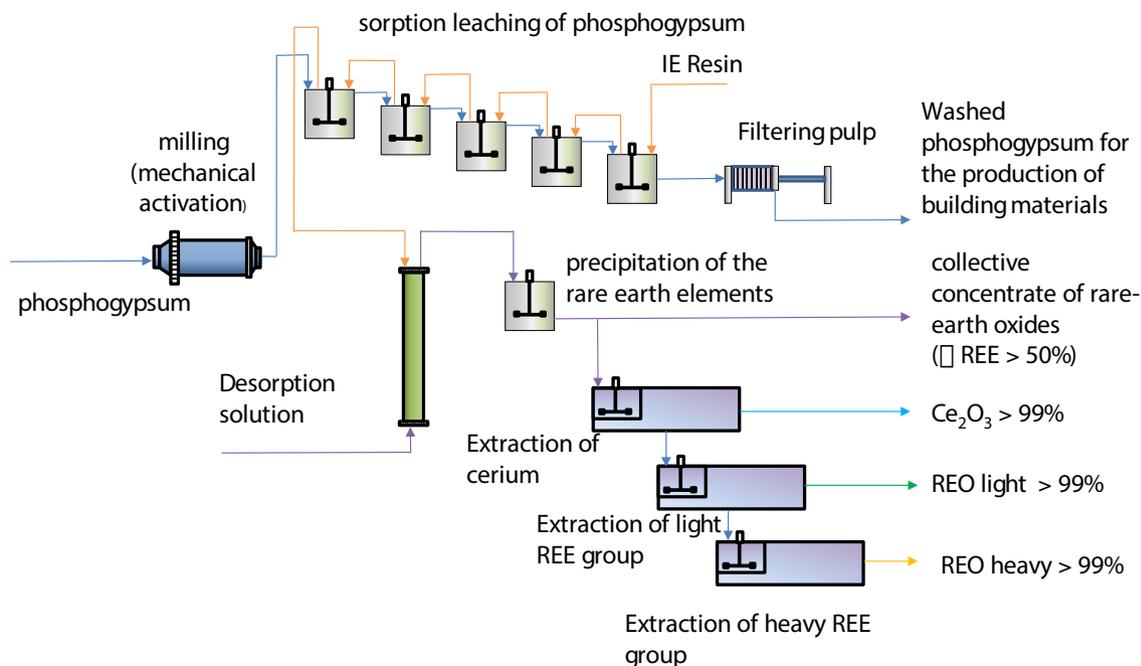


Figure 3. The technological scheme of countercurrent REE recovery from PG (above). Flowsheet process model of the countercurrent sorption process (below).

	Leaching efficiency (%)	Precipitation efficiency (%)	Total yield from raw material to precipitate (%)
La [%]	62.5	98.6	61.7
Ce [%]	77.0	99.0	76.2
Pr [%]	69.0	99.7	68.7



Table 4. REE enrichment into the solution and precipitate from NiMH battery waste. Figure shows the REE precipitate formed.

PG leachate amended with yeast extract and lactate donor using *Desulfovibrio desulfuricans* and mixed cultures are presented in Table 4. The result indicates substantial enrichment of rare earth metals in the formed SRB precipitate. New research (REE-PG) will pursue to enhanced volumetric efficiency of the SRB based technique. SRB

strains such as *Desulfovibrio*, *Desulfobulbus* and *Desulfotomaculum* will be isolated from environmental samples and cultivated, and their activity in different media containing PG sludge will be tested. The research commenced in 2016 will be conducted by VTT in co-operation with MINTEK biohydro-metallurgical division as part of

the REE-PG project led by Lappeenranta University of Technology and funded by Academy of Finland (Finland-South Africa co-operation).

### Recovery of REE from NiMH battery waste

REE recovery is of the global interest due to the geographical occurrence of the ore bodies, ca. 90% of the primary rare earth metals being produced in China. Currently, there is no REE recovery in Finland whereas in Europe, e.g., Umicore and Solvay (Rhodia) jointly recover also REEs present in the battery waste. METYK – project led by Aalto University focuses on REE recovery from NiMH battery waste. In Aalto University the focus is on investigating a straightforward hydrometallurgical method for REE recovery from NiMH battery waste utilizing industrial symbiosis present in the

Harjavalta Industrial Park. The focus of the REE research in the project has been in the leaching of NiMH battery waste in sulphuric acid lixiviant and the subsequent recovery of REEs from the acidic sulfate media. Table 5 shows the REE enrichment to the precipitate. The project has been conducted in collaboration with TEKES, EU and nine industrial and municipal partners.

## Conclusion

The inorganic waste heaps being compiled in large volumes in the metallurgical and fertiliser industries provide both environmental challenge in their storage and a potential urban mine having the “concentrate” already in a ready processed form for recycling their contents. Thus in environmentally conscious world striving for available sources of precious and critical metals the waste stacks appear as a rewarding target. The objective is to find means to reduce or remove the environmental footprint of problem waste storage and to find technically and economically viable means to recover their value-added contents. Jarosite and phosphogypsum are among the foremost examples of such utilisation.

The advantage of the ‘Jarogain’ concept is its energy efficiency as no thermal or mechanical processing is directed to the bulk mass. The step-wise hydrometallurgical treatment is aimed at high purity products with equally high yields. The process can be realised with conventional hydrometallurgical equipment (reactor-thickener-clarifiers). The leftover precipitate is sustainably lower in quantity compared to the original waste heap and will mainly consist of silicate gypsum without toxic components and can be used either as embankment fillings or even as construction material.

For the phosphogypsum processing, the treatment by countercurrent absorption allows the recovery of valuable rare earth metals. A more further off concept could be provided by the biological treatment, where absorption steps would then be replaced by bacterial activity and adjacent physico-chemical fractionation.

While the biochemical method has yet to be scaled up from small laboratory scale,

the absorption technique is attested robust, combining the best practices of resin-in-leach and conventional selective precipitation techniques. The operated minipilot appears as ‘proof-of-concept’ while giving fractionated REE concentrates. The economic operation of the rather complex process will depend on demand and price levels of rare earth applications. Yet, with their wide range of established uses in new energy techniques, mobile electronics, lasers, lighting and photonics, power transmission etc. the global demand most likely will but increase.

The NiMH battery waste is rich in base metals and REEs compared to inorganic waste heaps. Furthermore, the raw material volumes and equipment in the processing are smaller being closer to precious metal refinery scale compared to base metal production. Yet, to improve the circular economy of metals and to improve the independency in REE production, there is also nationally a need to development of REE recovery processes.

Both jarosite and PG treatments rely mostly on unit processes, whose technical feasibility has been proven in many applications before. Thus, with appropriate references gained in the ongoing research, the concepts can also be copied to treat the multiple similar sources around the globe. ▲

## Literature:

- Rastas, J.; Jarvinen, A.; Hintikka, V.; Leppinen, J.: Recovery of lead, silver and gold in the zinc process and possibility of non-waste technology in zinc production, VTT Symposium (1989), 103(Non-Waste Technol., Vol. 2), 235-51.
- Moors, E. and Dijkema, G.: Embedded industrial production systems - Lessons from waste management in zinc production, *Technological Forecasting & Social Change* 73 (2006) 250-265
- Kaksonen & Puhakka, Eng. Life Sci. 2007, 7, No. 6, 541-564
- Rathore & al.: Utilisation of jarosite generated from lead-zinc smelter for various applications, *Int. J. Civil Engineering & Technology*, 5 (2014), Issue 11, , pp. 192-200

- United Nations Environment Programme, (2013), *Metals Recycling Full Report*
- Koukkari, P., Mäkinen, J., Bomberg, M., Lehtonen, A. & Arnold, M. 2013. Method for recovering rare earth metals from waste sulphates. FI 125550 B, 30.11.2015.
- Kirillov, S., Kirillov, Y., Pajarre, R., Rychkov, V. and Koukkari, P: Recovery of Rare Earth Elements and Scandium as Side Products of Uranium and Phosphate Mining, *Konferens i Mineralteknik*, 2.-3.2.2016, Lulea, Sweden
- Larsson, K., 2012, *Hydrometallurgical Treatment of NiMH Batteries*. Göteborg : Chalmers University of Technology (Doktorsavhandlingar vid Chalmers tekniska högskola. Ny serie, no: ).
- Rollat, A., Guyonnet, D., Planchon, M., Tuduri, J., 2016, Prospective analysis of the flows of certain rare earths in Europe at the 2020 horizon, *Waste Management* 49, 427 – 436.
- Tunsu, C., Petranikova, M., Gergoric, M., Ekberg, C., Retegan, T., 2015, Reclaiming rare earth elements from end-of-life products: A review of the perspectives for urban mining using hydrometallurgical unit operations, *Hydrometallurgy* 156, 239 – 258.
- Yahorava, V., Bazhko, V., Khosa, G., du Preez, A., Mottay, R., 2012: Recovery of rare earths from phosphogypsum: development of the flowsheet up to refinery. Randburg, MINTEK.

## Acknowledgements:

- Academy of Finland:  
Grants nr 298094, 303453, 303454  
Raw Matters Finland Infrastructure (RaMI)
- TEKES:  
3089/31/2015 (JAROGAIN)  
3254/31/2015 (METYK)
- Ministry of Education and Science of Russian Federation:  
14.581.21.20002