Recovery of Copper, Iron, and Alumina from Metallurgical Waste by Use of Hydrogen

Casper van der Eijk and Halvor Dalaker

Abstract Substituting carbon with hydrogen is one of the few ways metal production can potentially become free of CO_2 emissions. Moreover, the metallurgical industry produces significant amounts of waste. The present work presents a circular concept that will be pursued in the HARARE project, based on increasing waste recovery by the use of hydrogen. The project will tackle two example cases: bauxite residue and copper smelter slags. The common theme is to use hydrogen to selectively reduce iron and copper, making it possible to extract these metals. Through a series of pyro and hydrometallurgical steps, as well as mechanical separation, it is also possible to recover secondary valuables like alumina, molybdenum, cobalt, nickel, zinc, and scandium. The final remaining residues can be valorised as building materials for a truly zero-waste concept. In this paper, the different process streams for the two example cases are laid out, including the valorisation of secondary material streams.

Keywords Hydrogen · Bauxite residue · Copper slag · Circular economy · Recycling

Introduction

The metallurgical industry is a large emitter of CO_2. In the EU27, it accounted for 162 million tonnes of direct CO_2 emissions in 2019 [1]. Of these, some 86 million tonnes are related to production of the energy used in the processes. While by no means trivial in practice, this energy can be replaced by emissions-free alternatives, and eliminating the energy-related portion of the CO_2 emissions is thus at least theoretically feasible with existing technologies. The remaining CO_2 emissions on the other hand—some 47% with EU numbers, and likely similar around the globe—are tied directly to the use of carbon in the industrial processes that turns ore into metal. Eliminating these emissions requires different processes from those of today, which is why metal production is listed as a "hard-to-abate sector" [2]. One of the

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few ways the process-related (i.e. non-energy) CO_2 emissions of metal production can be eliminated is to replace carbon with a different reducing agent, with hydrogen often being mentioned as the foremost candidate.

Another challenge of the metallurgical industry is the inefficiency that is found in its value chains. For example, 10–30% of the aluminium present in bauxite ore ends up discarded as bauxite residue (BR), and the discarded slags from copper smelting contain about 1% Cu—more than the concentration of Cu in ore from an average modern mine. These inefficiencies also indirectly increase the CO_2 emitted per ton of finished product, not to mention that they lead to waste problems, with millions of tonnes of metallurgical by-products piling up in landfills every year.

The HARARE project [3] (Hydrogen As the Reducing Agent in the REcovery of metals and minerals from metallurgical waste) will demonstrate sustainable pathways to produce metals using hydrogen as an enabler, for removing waste and valorising materials in carbon free processes. In this paper, we outline the proposed processes that will be investigated in the HARARE project.

Overall Concept

In both the slag from flash smelting of copper and the bauxite residue from alumina production in the Bayer process, the main component is iron oxide. At the core of the HARARE concept is the use of hydrogen gas to reduce the iron oxide to without process-related CO_2 emissions. Having removed the iron, the main components (copper and alumina, respectively) can be recovered and returned to their value chains. To ensure a zero-waste approach, potentially harmful elements must also be removed, and all other residues turned into useable resources like building materials.

The different approaches are outlined in Fig. 1.

The use of hydrogen for the recovery of metals from Cu slag and bauxite residue has already been described in literature. But for the case of copper, the emphasis was on raw materials rich in copper [4]. When bauxite residue is treated with hydrogen at temperatures above ca. 850 °C, hercynite ($FeAl_2O_4$) is formed [5]. The formation of this phase makes the separation of aluminium and iron difficult. So either the reduction temperature must be kept low, accepting that the iron oxides will not be

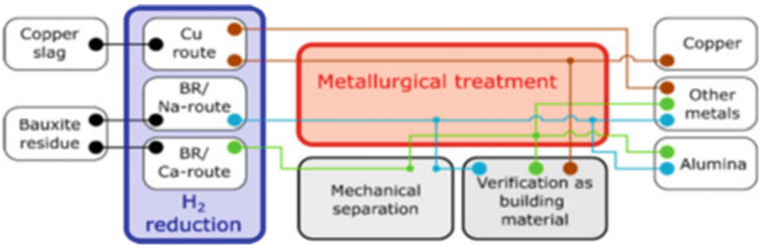

Fig. 1 Sketch of the overall idea

reduced to metallic iron but to magnetite (Na-route in HARARE) or Ca must be added leading to the formation of the Ca-Al-oxides which are more stable at high temperatures than hercynite (Ca-route in HARARE).

The Injection of Hydrogen to Refine Copper Slags

Slag from copper flash smelting contains not only slag-forming components, but also copper levels comparable to that in ores from modern mines (~1 wt%). In addition, it contains iron oxide (~50 wt%), alkalis and heavy metals (K, Na, Zn, Pb++, ~3–5 wt%), as well as smaller amounts of molybdenum, cobalt and nickel. The high iron content of the slag makes it challenging with traditional methods to extract the copper without also extracting a lot of iron and creating a low-Cu high-Fe alloy of little commercial relevance. Even without copper recovery, the alkalis and heavy metals make it difficult to valorise the slag as a construction material or as an iron source. The low-value options available for slag valorisation are as blast abrasion agent, cement compound, and river embankment. The slag is partly valorised through these means, but volumes are limited. Furthermore, legal limits for heavy metals will be lowered in the future, further restricting the opportunities available.

In HARARE, RWTH Aachen and Aurubis will develop selective reduction process based on hydrogen injection into the liquid slag. Using hydrogen as the reducing agent allows the reducing potential to be fine-tuned with the composition of the gas and the process temperature, controlling which metals will be reduced. The expected selectivity is up to 2,27 mCu/mFe in the metal phase. A Sankey diagram of the process is shown in Fig. 2. The process will have two steps:

- Step 1, lower reducing potential:

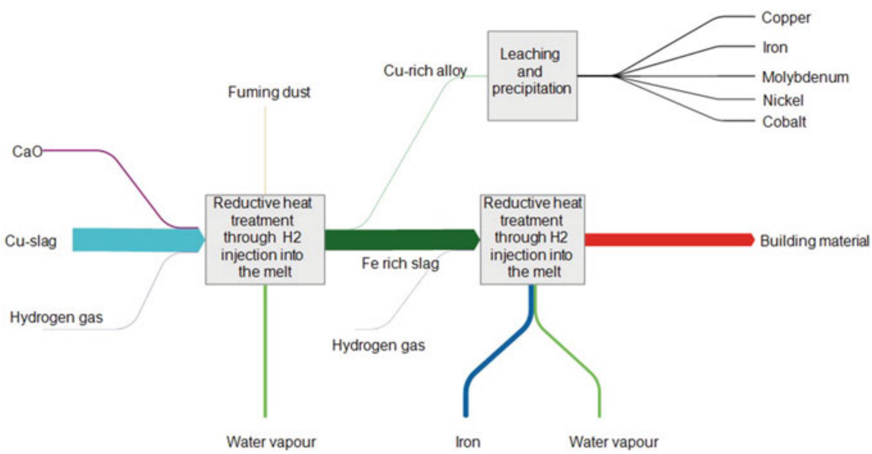

Fig. 2 Sankey diagram for the valorisation of copper slag

  - Copper will be reduced to liquid metal alloy along with smaller amounts of Fe, Mo, Co, and Ni.
  - Alkalis and heavy metals will be reduced to metallic fumes and collected as flue dust,
  - Iron will mostly remain in the slag in its oxidised state.

- Step 2, increased reducing potential:

  - Iron oxides are reduced to iron and removed as pig iron.

This process will separate the different valuable components of the slag and create the following products;

- High-value high-copper alloy.
- Pig iron
- Zn-rich flue dust as raw material for Zn production
- Slag free of iron, alkalis, and heavy metals, suitable as a construction material.

Recovery of Alumina from Bauxite Residue

In the production of aluminium, almost twice as much bauxite residue (BR) as aluminium metal is produced. Despite containing potentially valuable materials such as aluminium, silicon, and iron, as well as rare earth elements (REEs), BR is mostly landfilled. This is not only a waste of resources, but also presents a land-use problem, as BR takes up increasing amounts of land.

The iron oxide in the BR can be turned into iron by hydrogen reduction. In order to facilitate recovery of alumina and valorisation of other residues, fluxing of the BR prior to H_2 reduction is necessary. In the HARARE project, two routes for BR processing are pursued. The first route the "Ca-route", uses CaO as a flux, while the second route, the "Na-route", uses NaOH.

The Ca-route works at high temperature and thus fits best for BR qualities that are low in Ti because the Ti binds with Al in a perovskite structure at high temperatures. The Na-route on the other hand can tolerate BR qualities with high Ti, since it takes place at lower temperatures. Furthermore, the final residue of the Ca-route is easier to use as building material because with Ca-silicate content, it resembles normal cement. The two routes are described below.

Calcium Route for the Recovery of Alumina from BR

In the calcium route, NTNU and SINTEF will treat BR by hydrogen together with CaO to produce iron and a tailor-made slag of CaAl-oxides (mayenite) that is leachable at low temperatures. A Sankey diagram of the process is shown in Fig. 3. The process will take place below the melting temperature of iron, which means that the produced iron will be in the solid state and thus cannot be separated by a tapping

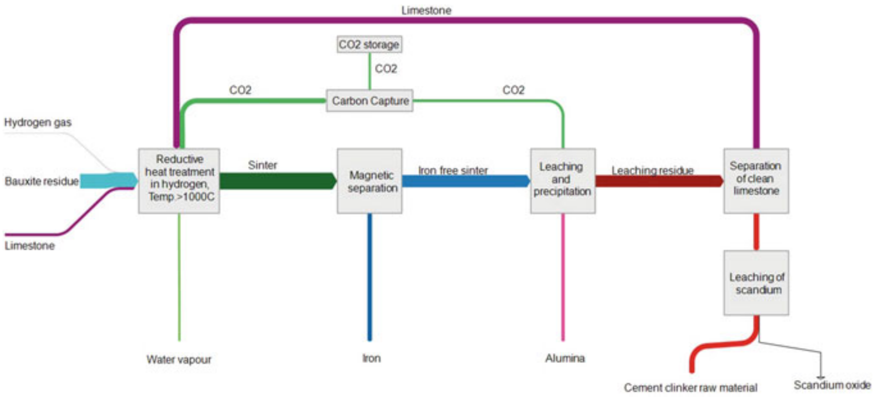

Fig. 3 Sankey diagram for the valorisation of BR through the Ca-route

process. The separation of the solid iron particles is one of the challenging parts of the process because the distribution the iron particles in the oxide is very fine. NTNU and ReSiTec will test different crushing, grinding, and separation techniques to liberate the metallic from the non-metallic phases, including magnetic separation and floatation.

After separation of the iron, the non-magnetic fraction will consist mainly of an easily leachable alumina-containing slag (mayenite). The alumina will be leached from the mayenite by NTUA, and Al-hydroxide will be precipitated from the solution and can be returned to the aluminium value chain.

The remaining residue at this stage is rich in limestone which will be recovered by flotation at NTNU to be recycled to the start of the process chain for a new roasting stage. During the roasting stage, CO_2 is generated from the limestone during the reductive treatment. The off-gas is a mixture of CO_2, H_2O, and unreacted H_2. From this gas mixture, the CO_2 can be easily concentrated.

Most of the CO_2 is reused in the process when the CO_2 is needed during precipitation, whilst the CaO is turned into $CaCO_3$ again. The CO_2 concentration for precipitation does not need to be 100%, so here is a possibility to use a diluted CO_2 stream from another industrial process while the concentrated CO_2 from the heat treatment is stored. The capture and storage of CO_2 is a possible add-on to the process which will not be included in the HARARE project work.

After the recovery of the limestone, the remaining residue consists of oxides suitable for use in building material, into which the Sc and other rare earth elements (REEs) in the BR will also have concentrated.

Sodium Route for the Recovery of Alumina from BR

BR can be recovered by roasting with carbon, smelting, and leaching [6]. Based on this work, KU Leuven will develop the process further into an electrically heated,

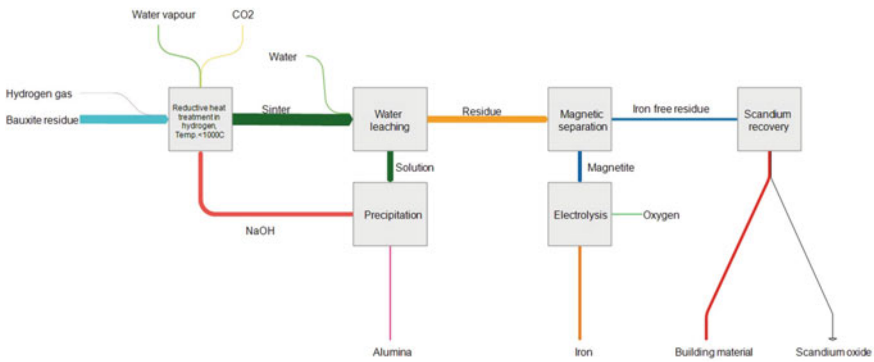

Fig. 4 Sankey diagram for the valorisation of BR through the Na-route

H_2-based reduction process, with no smelting. A Sankey diagram of the process is shown in Fig. 4.

Step (i) is alkali roasting of the BR with NaOH in H_2 atmosphere. This treatment will turn the aluminium oxide in the BR into water soluble $NaAlO_2$ and reduce the iron oxides. The temperature is lower in the Na-route than in the Ca-route, which means that the iron oxide is not reduced to metallic iron, but rather to magnetite, Fe_3O_4.

Step (ii) is water leaching. Sodium and aluminium will dissolve as Na^+ and Al^{3+} and can then be precipitated as hydroxides. $Al(OH)_3$ is returned to the aluminium value chain, while NaOH is recycled to the start of the Na-route and used with a fresh batch of BR.

The solid fraction in the leaching step consists of magnetite and a non-magnetic oxide-phase. These are separated by wet magnetic separation and can be used as raw material for iron and building materials respectively. Once again, the REEs of the BR are expected to be concentrated in the oxide residue (Fig. 4).

Secondary Material Streams and Zero-Waste Approach

The main focus of the HARARE processes is on the recovery of copper and alumina back into their respective value chains, but in a completely zero-waste approach, every material stream will be valorised. Some details on the approaches to valorise the secondary material streams are described below.

Separation of Copper-Alloy

The Cu-rich alloy produced from the copper slag also contains other metals like Fe, Mo, and Co. These can be separated through hydrometallurgical, electrometallurgical, or pyrometallurgical treatment. The best option will depend on the composition of the alloy, which is not only produced to maximize the Cu content in the alloy, but also to minimize the Cu lost to the slag. NTUA will perform the hydrometallurgical treatment and electrometallurgical treatment, which are both based on dissolution followed by selective precipitation, while NTNU will perform pyrometallurgical treatment based on vacuum refining.

Rare Earth Elements, Scandium

BR contains significant amounts of REEs, in particular scandium. In both the Ca-route and the Na-route, these valuable materials are expected to concentrate towards the non-ferrous oxide-phase after recovery of the alumina- and iron-rich phases.

From the Ca-route, NTUA will treat remaining oxide-phase after limestone recovery with mineral acids (HNO_3, HCl, or H_2SO_4) and ionic liquids to recover REE and Sc by selective leaching.

From the Na-route, the non-magnetic leachate is a mixture of an amorphous silica-rich phase and a perovskite ($CaTiO_3$) which contains most of the scandium and REE. By dissolving the silica-phase at high temperatures and pressures, KU Leuven will recover the valuable $CaTiO_3$ phase, an "artificial deposit" of REE.

Zn and Pb from Flue Dust

During the hydrogen treatment of the Cu slag, the volatile metals Zn and Pb will end up as oxides in the flue dust. The recovery of zinc and lead from such oxidic powders is part of the common, industrial zinc winning and recycling practices. There, zinc metal or oxide is leached with sulphuric acid, while lead oxide stays unsolved or metallic lead precipitates as lead sulphate. RWTH will demonstrate that the recovered flue dust from the HARARE process is compatible with these recovery techniques.

Electrolytic Refining of Iron from Magnetite

The magnetic phase at the end of the Na-route is rich in magnetite, Fe_3O_4, but cannot be used as a raw material in blast furnaces due to its high Na content. NTUA will use it as a raw material for electrolysis of iron, by using a process similar to that developed in the Horizon2020 project called SIDERWIN [7] in which NTUA and Mytilineos are partners.

Building Materials

Even with the substantial efforts of product- and by-product valorisation, significant fractions from the HARARE value chain will remain as non-metallic residues. In order to determine the best way to valorise these as building materials, KU Leuven will correlate the structure of the residues with their predisposition for dissolution through reactivity protocols, produce high-performance alkali-activated or blended cements, and deliver predictive models on the properties of the binders.

To demonstrate that there are no adverse effects on the surrounding environment of using these materials in construction, SINTEF will investigate the leaching of harmful substances from the valorised residues.

Outlook

The HARARE project offers innovative solutions for materials streams that generate over 160 Mt/year of residues that are either landfilled or used for low-end applications (2020 data). Furthermore, these streams contain valuable metallic and non-metallic phases that are not valorised in any way. The solutions proposed in Harare are based on hydrogen, will thus be free of process-related CO_2 emissions, and look very attractive from an environmental perspective. The ecological sustainability will be verified through LCA, lead by AdMiRIS. Since a positive environmental impact is not sufficient for real-world implementation, AdMiRIS will also evaluate techno-economic viability and value creation assessment, together with SINTEF.

To some members of the general public, hydrogen is associated with safety concerns and fear of explosions. In developing the concepts described herein, both in the laboratory and pilot scale, the expertise of Linde will ensure that such risks are managed in a responsible manner, and that the processes will be safe. Communications of results will be aimed at the general public by popularizing the information in national and local media as well as in social media including screen casts and videos. This will raise awareness among the general public about the applications, potential, and benefits to society of the developed technologies.

The project kicked off in June 2021 and will run for 48 months. We look forward to publishing results as they become available.

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