HYDROMETALLURGY AND PHYTOMANAGEMENT APPROACHES FOR STEEL SLAG MANAGEMENT (HYPASS)

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Introduction

Steel slags are major by-products produced by the steel and iron industry. While they are considered as industrial waste, slags represent an important potential economic resource because they often contain significant amounts of valuable "Strategic Metals" (SMs). These metals are essentially used as alloying elements in the steel industry as well as in catalysts and pigments in the chemical industry and as raw material in green technologies (photovoltaic cells, wind turbines and electric motors). During the last decade the global steel production driven by China has doubled and the development of renewable energies (wind and solar) and electrics cars has dramatically increased. This has sharply affected global SMs demand, and there is no doubt today that production and consumption of SMs will face a major economic pressure in upcoming years. In this context, the importance of hydrometallurgy in production and recycling of SMs cannot be stressed enough. However, improving or even optimising these processes is clearly required. In addition, although steel slags are classified as non-hazardous thermal waste according to the decree 2002-540 and the United States Environmental Protection Agency, it is well known that most metals they contain are quite toxic to living organisms and may pose serious environmental issues. In France, the "Centre Technique de Promotion des Laitiers sidérurgiques" (CTPL) estimated that the total available stock of slags (including all slag families) was about 17 480 600 tons at the end of 2015. Thus, reusing steel slags appears the option of choice to ensure their sustainable management as well as to decrease their environmental concerns.

The HYPASS project

The goal of the HYPASS project, funded by the "Agence Nationale de la Recherche" (ANR), is to propose technological innovations for both a cost-effective recovery of strategic metals and an eco-friendly management of metallurgical dumps. In this respect, HYPASS will consider the process as a whole, from by-products production to slag valorisation and finally rehabilitation of contaminated landfills, with the ultimate goal of developing economically feasible and environmentally acceptable "zero-waste" processes. The core of the project is the development, assessment and evaluation of two complementary valorisation routes using: 1) hydrometallurgical-based approaches (under alkaline conditions) to recover high SMs amounts, and 2) phytostabilisation approaches [and the beneficial role of "*Arbuscular Mycorrhizal Fungi*" (AMF)] to promote ecological restauration of slagheaps. Additionally, HYPASS proposes to list and to map existing dumpsites, to perform "Life Cycle Assessments" (LCA) for various processing methods and to develop a "Decision-Support Tool" (DST) to help identifying the best treatment options, both from an economical and from an environmental point of view. HYPASS technologies are implemented since January 2018 at a large slagheap situated at Châteauneuf (Loire, France) with an estimated stock of 500 000 tons of "Electric Arc Furnace" (EAF) slags, whose principal SMs are: Cr_2O_3 (± 2.4%), V (± 1500 ppm), Mo (± 500 ppm) and Zn (± 500 ppm).

The metals, oxides and/or hydroxides recovery from slags has long been, and still is, the subject of numerous studies. Today, a number of technical options are available to extract SMs from contaminated mineral matrices (such as slags). The techniques implemented are generally using the principles of hydrometallurgy and involve mechanical, magnetic, chemical[1] and/or physicochemical (flotation) separation processes in various combinations[2]. In the ANR ECOT ORLA, ERA-MIN EXTRAVAN and HORIZON 2020 CHROMIC research programs, successful comminution techniques have been explored. Mechanical processing technologies that can be used are: smart fragmentation with a rotating drum, smart magnetic, reverse magnetic and high gradient magnetic separation for magnet material and electrostatic separation for fine particles. Up to now, the solutions reported in the literature for the dissolution of the metallic parts are almost exclusively by an acid route.[3] Incorporated into mineral matrices and sometimes committed in the form of ferrites type, SM-based non-ferrous oxides (Cr, V, Mo, *etc.*) have rarely been the subject of specific treatments. However, when keeping the mineral matrix intact is desired for its subsequent valorisation, processing technologies using acid leaching are inapplicable and clearly to be avoided. During acid leaching, the release of lime presents a major inconvenience. Hence, this causes overconsumption of reagents and an excess of salt production. By contrast, the alkaline environment (soda ash, ammonia, *etc.*) offers several advantages. Particularly, soda ash’s weak corrosion power and selectivity has

many benefits. Iron and calcium, present in slags, are poorly leached at the end of alkaline treatment. Moreover, adding lime in a soda ash solution precipitates the silicates and carbonates and thus returns the leaching solution to its initial state. Precedents for the alkaline process[4] proposed exist but they differ from this proposal as they were applied on substantially different materials (steel dust or metal hydroxide sludge) with REZEDA® and EZINEX® processes. Notice: the utilisation of alkaline solutions for SMs recovery from slags is in itself innovative. Even if the nature of the mineral by-products is foreseeable ["Calcium Silicate Hydrate" (CSH), brucite, Si-Al gels, *etc.*], neither their grain-size distribution nor the yield of metal recovery are easily predictable or completely understood. Thus, the hydrometallurgical challenge is to evaluate the alkaline process, for which the major scientific problem is to predict properties of the precipitated solids (crystallisation).

The main objective of HYPASS is to propose new approaches for an eco-compatible and sustainable slag management, and not to simply recover SMs from primary slags, while generating secondary waste. Therefore, HYPASS includes the "downstream" environmental concern of the fate of slags and secondary waste products. If some slag types are not relevant matrices for hydrometallurgical processing or if the resulting secondary mineral matrix does not meet the environmental acceptability criteria for a safe use in the field of civil engineering, HYPASS will implement a containment strategy for limiting wind and water erosion of metallurgical dumps and to prevent leaching and run-off of contaminants. In a context of increased awareness of the importance of soils as a finite and non-renewable natural resource, capping of metallurgical dumps using a geo-membrane liner covered by a layer of clean soil is definitely not the best option, neither economically, nor environmentally. By contrast, pollution containment using aided-phytostabilisation is a growing field of research and a relevant approach for the sustainable ecological management of large polluted sites.[5] As such; phytostabilisation relies on concepts and approaches that are now quite common. However, its application for on-site management of metallurgical waste dumps has never been implemented to date. In fact, the establishment of a plant cover onto steel slagheaps must overcome a number of issues. First, besides the potential toxicity of metal elements (*e.g.*, Cd, Cr, Mo, Ni, Pb, *etc.*), slags are almost devoid of organic matter and essential macronutrients (N, P, K). They also have very low water holding capacity and a high pH (> pH 9), that greatly reduce the phyto-availability of essential trace metals (*e.g.*, Fe, Cu, Zn). Second, steel slags can hardly fulfil the functions of a living soil (*i.e.*, nutrient cycling, organic matter decomposition, carbon sink, habitat for biodiversity, *etc.*), as they lack most, if not all, of the key engineer species (bacteria, fungi, protozoan, nematodes, annelids, arthropods, plants, *etc.*) involved in soil biological processes. Therefore, these overall very particular characteristics make metallurgical slags a very bad substrate for plant development. However, Bouchardon demonstrated [at an experimental plot field

scale (50 m^2 plots)] that phytostabilisation of slag dumps was still feasible, provided to use an appropriate organic fertilisation and an adapted plant community. Although the methodology proposed was successful in obtaining a dense plant cover that reduced pollutant transfer *via* wind erosion by almost 95%, some metal elements and, particularly, those forming oxyanions (mainly, Cr and Mo) were accumulated in above ground plant parts at relatively high levels. Therefore, decreasing Cr and Mo accumulation in plants used for phytostabilisation of slag dumpsites remains an important research issue. In this respect, a key factor for the success of phytostabilisation of steel slags could rely on stimulating the development of an active and diverse soil microbial community. Among the huge diversity of soil organisms, the beneficial role of AMF as promoting factors for plant establishment, is increasingly acknowledged, both for agricultural practices and for phytostabilisation purposes. AMF establish symbiotic associations with plants roots thereby improving mineral nutrition and water acquisition of their host. In addition to a better tolerance to soil nutrient deficiencies and drought stress, there are a growing number of evidences that AMF may decrease the accumulation of toxic metals in plants[6] and particularly Cr, thus improving the efficiency of phytostabilisation. Starting from these results, HYPASS will precise the best conditions for an efficient phytostabilisation both of primary slags and of secondary mineral matrix resulting from the hydrometallurgical process.

References

1. M. L. Cunha, C. S. Gahan, N. Menad, A. Sanström, "Possibilities to use oxidic by-products for precipitation of Fe/As from leaching solutions for subsequent base metal recovery", *Miner Eng*, **21** 38-47 (2008).
2. P. E. Charpentier, L. Rizet, C. Trouillet, "Traitement d'extraction des métaux lourds - Techniques de l'Ingénieur", IN70, 12 p. (2008).
3. Z. Yang, M. Rui-Lin, N. Wang-Dong, "Selective leaching of base metals from copper smelter slags", *Hydrometallurgy*, **103** (1-4) 25-29 (2010).
4. E. Kima, J. Spooren, K. Broos, L. Horckmans, M. Quaghebeur, E. Vrancken, "Selective recovery of Cr from stainless steel slag by alkaline roasting followed by water leaching", *Hydrometallurgy,* **158** 139-148 (2015).
5. M. Mench, N. Lepp, V. Bert, J. P. Schwitzguebel, S. W. Gawronski, P. Schröder, J. Vangronsveld, "Successes and limitations of phytotechnologies at field scale: outcomes, assessment and outlook from COST Action 859", *J Soil Sediment*, **10** (6) 1039-1070 (2010).
6. E. Orlowska, D. Orlowski, J. Mesjasz-Przybylowicz, K. Turnau, "Role of mycorrhizal colonization in plant establishment on an alkaline gold mine tailing", *Int J Phytoremediat*, **13** 185-205 (2011).