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Review

Three-liquid-phase extraction in metal recovery from complex mixtures

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A B S T R A C T

Modern metal production techniques often use solvent extraction either for separation or purification purposes. Processes were developed for specific mineral ores and deserve consequent modifications to be adapted to the recovery of metals from complex mixtures, arising eg from the hydrometallurgical processing of waste of electrical and electronic equipment (WEEE), as these mixtures contain a large panel of elements in highly fluctuating content. Three-liquid-phase (TLP) extraction systems allow the separation of metallic ions in three different phases in a single apparatus, and thus open the door to the treatment of complex mixtures with fewer operations. This paper reviews the work performed on TLP systems for metals separation, and highlights the potential advantages of such a technique in the design of new processes. Several systems enable the controlled formation of three immiscible phases, and have been successfully applied to the separation of various metals of interest. Advantages and drawbacks of each system are discussed, with a perspective for further developments, and the possibility for the rapid sorting of complex mixtures into separate groups of metals, easy to process.

1. Introduction

Liquid-Liquid extraction (or solvent extraction) is one of the key techniques operated at industrial scale for the separation and purification of metals. It complements well pyrometallurgy, and is routinely employed during the production of various metals such as copper, cobalt, nickel, rare earths or Platinum Group Metals (PGMs) from natural ores. This technique is also more and more considered for the recovery of metals from secondary resources, such as low grade ores, and waste with a high valuable metal content, such as waste of electrical and electronic equipment (WEEE) found in the so-called urban mine [1]. In the latter case, liquid-liquid extraction processes have been developed at lab or pilot scale for the recovery of various metals, such as gold, PGMs, tantalum or indium [2–4]. However, according to recent studies [5], less than 10% of the overall WEEE are recycled, and landfill disposal is preferred. This statement is generally striking considering that WEEE contain valuable metals at ten to hundred fold higher concentrations than natural ores, which are of lower and lower quality [6,7]. Among the reasons to account for the low recycling rate of metals from wastes, complexity of the proposed processes may be at the top. This complexity originates in two real issues associated with WEEE reprocessing: WEEE generally contain hazardous substances, and a very large number of different metals to separate [8,9]. Hazardous substances are principally organic halogenated compounds, especially chlorinated and brominated aromatics, employed as flame retardants in the thermoplastic components or for cable insulation. They are persistent substances of high concern for environmental and human health, and/or generate toxic dioxins upon incineration, which limits pyrometallurgical treatment [10,11]. The metals found in WEEE are very heterogeneous. This implies a very high number of steps required to separate all these metals, with a consequent generation of process wastes. Altogether, although hydrometallurgical treatment of WEEE appears as a market of vast potential, efforts are needed to develop efficient and compact processes. Three-liquid-phase (TLP) extraction appears as an emerging alternative. This strategy relies on the use of three immiscible liquid phases, and generally involves one aqueous feed and two extraction media (organic solvent, ionic liquid, etc.). Still in its infancy, the technique opens however interesting perspectives in the treatment of complex mixtures, as three metallic cations instead of two can be separated simultaneously in a single step. In this paper, we propose a critical review of the existing TLP systems proposed to perform metals separation, and discuss their advantages and drawbacks regarding to conventional solvent extraction.

2. Hurdles in metals isolation and separation with hydrometallurgy from complex mixtures

There are many different secondary resources which contain metals. Whereas some are of simple and stable composition, most secondary resources are of fluctuating composition, and contain a large number of

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different metals. In the former category, there is no particular issue regarding metal isolation or purification, and industrial process have been developed for the recovery of diverse metals such as zinc, copper, cobalt, nickel, cadmium, vanadium or molybdenum from various sources such as acid effluents, electroplating baths, metallic dust, fly ash, scrap alloys or spent desulfurizing catalyst [12,13]. More recent developments include, for instance, catalytic converters reprocessing towards PGMs recovery [14], or indium recovery from liquid crystal displays (LCDs) screens [15]. Also, simple flowsheets for nickel and cobalt recovery from batteries have been proposed [16]. On the other hand, electronic equipment such as mobile phones, computers, laptops, TVs, etc. contain numerous metals such as copper, iron, aluminum, tin, gold, silver, palladium, lead, zinc, etc. Furthermore, the content in each metal has been proven to be highly fluctuating since batches of wastes vary significantly, both in quality, as some metals are not always present, and in quantity, as metals contents are never stable [2,17]. Management of this chemical complexity is one of the major hurdles to overcome, if not the major one. Physical separation techniques have been implemented to collect fractions of elements of reduced complexity: plastics separation from metals, ferrous separation from non-ferrous, etc. In any case, it seems unlikely to circumvent dissolution and further separation of the metallic cations from the solution with hydrometallurgy.

As total dissolution with strong mineral acid or base leads to very complex mixtures, various selective leaching processes targeting some specific metals have been developed [8], including bio-leaching processes [18]. Most attention has been set on gold [19], the highest value source, and copper [20], present in very high content. Selective and complete leaching in these complex systems is a real challenge; therefore the leaching operation is always followed by an extraction and purification process. And generally most other metals are discarded, and an important effluent quantity is generated. A recent review [21] highlights the significant progress in the frame of printed circuits boards (PCBs) recycling. The best reported recovery yields for precious (e.g. Au, Ag, Pd) and some common important metals (e.s. Cu, Fe, Zn, Ni) are not always high, and very valuable metals such as Pt, Nb, Ta, Bi or Ga are almost often left aside. The principal reason is probably to be found in the hydrometallurgical strategy employed: processes are designed in order to isolate successively the targeted metals, one after the other, in a linear process.

Numerous extracting molecules have been developed and studied depending on the required purification to achieve [22–24]: spent nuclear fuel reprocessing, copper ore refining (Lix®), PGMs separation process (alamine 336®), rare earths separation, etc. Processes were specifically designed for well-defined metal feeds, and the number of steps can be very high as the number of metals to separate becomes important. For example, rare earth elements (REEs) purification flowsheet used at industrial scale by Solvay (former Rhône-Poulenc, Fig. 1) necessitates around fifteen distinct operations (each comprising several stages) for the preparation of rare earth oxides, as each REE is extracted one at a time [24]. Also, when separation factors are quite low (for instance around 3 in this REE process) the number of separation units tends to grow. Thus, 1 500 stages are reported in the case of the whole Rhône-Poulenc REE process, or 26 in the case of the related Molycorp process to produce sole lanthanum [24]. Modification of such specialized processes towards the reprocessing of wastes is conditioned to the sorting and dissolution steps, so that the feed to purify perfectly fits with the feed obtained from the natural ore.

The adaptation of existing techniques and processes deserves thus continuous efforts, but alongside the solution to the design of an efficient recycling of WEEE may arise from new extracting molecules or new extraction processes. In the latter case, separation of metallic cations into groups prior to final separation and isolation emerges as a new strategy. A quick sorting into a reasonable number of homogeneous families of metallic cations, easily manageable with existing techniques, appears thus as an interesting approach, rather unexplored so far. The idea has been present in the mind of scientists for decades: careful examination of the Rhone-Poulenc REE process reveals separation of some lanthanides as pairs, eg. Nd/Pr, which enables thus the direct production of didymium, or Sm/Eu, so that the process is not strictly-speaking a linear process. And it has also been applied in pyrometallurgy since its beginnings: base metals such as Cu, Pb or Ni are employed as collectors for precious metals (Ag, Au, Pd, Pt, Rh, Ir and Ru) and special metals such as Bi, Se, In, Sn and Sb; this is the basis of the Umicore process for WEEE recycling for instance. TLP extraction, composed of an aqueous feed and two extracting phases all immiscible, can provide straightforward solutions, as three flows instead of two can be generated during a single step. This strategy can be envisioned either for single metals separation, or included in a 'group separation' strategy.

3. Principles and benefits of three-liquid-phase solvent extraction

During a classical solvent extraction process, an aqueous metal-loaded feed is contacted with an immiscible organic solvent meant to extract selectively one metal in order to isolate and purify it, thus forming a biphasic system. Oil and water biphasic systems have been known for millennia. They were used, if empirically, for various extraction and purification purposes such as perfumes or medicines preparation [25], and of course metals separation. Such immiscible biphasic systems offer multiple opportunities for separation processes since the properties of the extracting phase can be easily tuned for the extraction of a specific compound, as illustrated before. Theoretically, increasing the number of non-miscible phases greatly reduces the number of distinct steps necessary for multicomponent feeds purification. A theoretical example is given in Fig. 2 in the case of a five metals input. In the case of a biphasic system, the metal with the highest affinity for the extracting phase is removed first, then a second is removed, etc. Processing as such, four successive operations have to be performed to separate five metals. Having three phases in contact, two metals for which the two extracting phases have an affinity can be removed in a single operation. Therefore only two successive operations are necessary in the case of a TLP system.

Working with three phases already offers relevant technological solutions in oil recovery processes and in industrial processes such as caprolactam production [26]. Latter cases usually involve the presence of an electrolyte in a high concentration, which induces segregation of otherwise miscible organic compounds. Three-phase partitioning also offers efficient solutions for the rapid isolation of organic macromolecules such as cellulose, enzymes and proteins [27]. Those molecules segregate in a phase distinctive from water and oil, and is thus purified from salts and low molecular weight organic impurities. In a similar approach, TLP systems have been developed for the straightforward separation of organic compounds, eg during the extraction of natural products from plants [28]. All these processes exploit a physical property (charge density, molecular weight) to segregate a class of compounds into a third liquid phase, obtained in a straightforward manner from the initial system. Finally, applications are also found in analytical science, although in this case generally two different miscible phases are separated by a third immiscible phase impregnated in a hollow fiber that enables the segregation into three distinctive compartments [29].

The shortening of solvent extraction flowsheets is a very important goal to achieve in order to develop efficient metal recovery processes. Indeed, each separation stage is generally accompanied by a scrubbing stage, a stripping stage and a solvent regeneration stage. Latter stages are also necessary in the processing of each phase obtained after phase separation in a TLP system. But as the complexity of these stages is strongly related to the complexity of the considered feeds, a rapid separation of the different metals present in the initial mixture leads to much higher flexibility in the design of the scrubbing and stripping stages (chemical reagents employed, volume ratios.). For instance, in