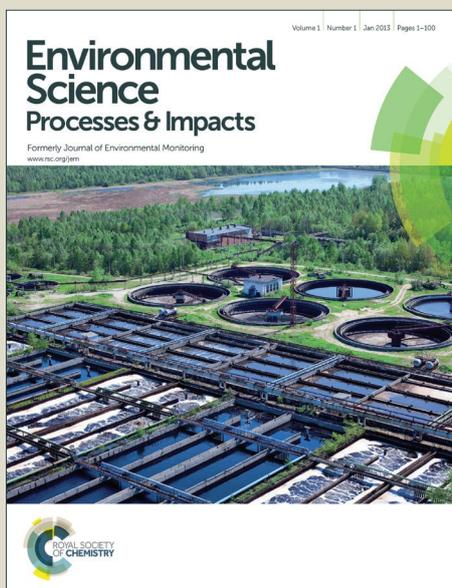


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## Environmental impact statement

Mechanochemistry has been introduced to recover metal from waste since 1990s and has successfully achieved the recovery of Pb, Li, Co, In, Cu, Au, Mo, Ni and rare earth up to now. Considering its being highly-efficient, environmentally-friendly and second-pollution-free, mechanochemistry is promising to expand its utilization to many other metals' recycling in order to relieve the shortage of metal resources.

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# Application of mechanochemistry to the metal recovery from second-hand resources: a technical overview

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In the context of huge imbalance between increasing demand on metal and the finiteness of metal resource in nature, recycling metal from second-hand resources, especially e-waste, is of great importance, to embrace the sustainability challenge. Inspired by hundreds' use in extractive metallurgy, mechanochemistry has been introduced to recover metal from waste since 1990s. The mechanochemical recycling process is technically feasible to recover metals from waste to a high yield, such as Pb recovery from cathode ray tube (CRT) funnel glass, Li and Co recovery from lithium-ion batteries, rare earth recovery from fluorescent lamps, In recovery from LCD screens, Cu recovery from waste printed circuit boards Au, Mo and Ni recovery from waste. Particle size reduction, specific surface area increase, crystalline structure decomposition and bond breakage have been identified as the main changes induced by the mechanochemical processes in the studies. Also, the activation energy required decreases and reaction activity increases, subsequently. This paper presents a technical overview of the applications of mechanochemistry to metal recycling from wastes. The current application pattern, reaction mechanisms, equipments used, method procedures, and the future research direction are discussed in detail. This work presents the limitation of current mechanochemical application in metal recovery and gives a perspective of the future development of mechanochemistry as well.

## Introduction

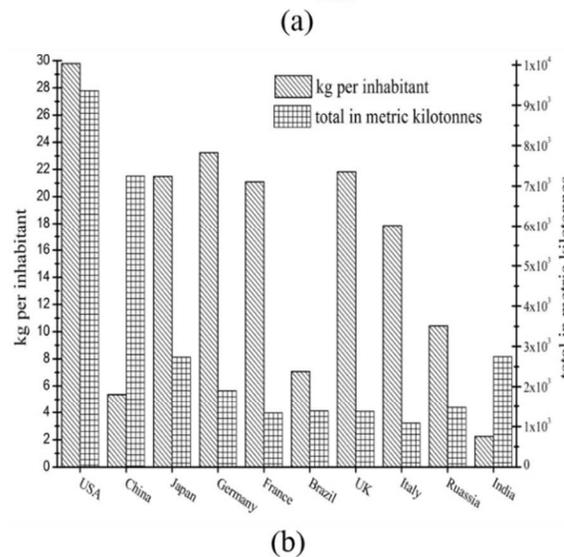
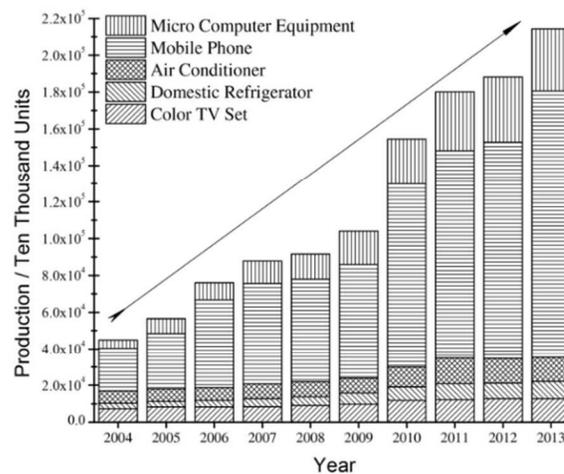
The past decades have witnessed a huge upsurge in mining metal from virgin ores to meet the demand in the burgeoning global market where consumption of new high-tech products containing various kinds of metal, no matter base, precious or specialty, as essential components, prevails.<sup>1, 2</sup> But metal in nature is finite anyway. It was estimated that, based on the comparison of the global mine production and the reserve base, copper in minerals would be drained in 61 years, lead in 43, zinc in 46, tin in 53, mercury in 80, nickel in 100.<sup>3</sup> At the same time, metal recycling is often inefficient or essentially non-existent: end-of-life recycling rates (EOL-RRs) for the commonly used "base metal" (iron, copper, zinc, etc.) are merely above 50% (these rates are the highest among sixty tested metallic elements).<sup>2, 4</sup> In view of the big imbalance between, the issue on metal sustainability has been brought to the forefront more and more.

The quantity of metal-containing waste is enormous. Set waste electronic and electrical equipment (WEEE), one of the most typical metal-rich second-hand resources, as an example.

According to the 2004-2013 data from China's National Statistics Bureau (CNSB) (as shown in Fig. 1 (a)), the past decade witnessed an enormous increase in the production of five types of electronic and electrical equipments (EEEs), including computers, cell phones, air conditioners, domestic refrigerators and colour TV sets, from 448.65 to 2,143.16 million units. It is widely accepted that WEEE or e-waste has been recognized as the fastest-growing component of solid-waste stream.<sup>2, 5</sup> The e-waste world map, which was portrayed by StEP (Solving the E-waste Problem), shows that almost 48.9 million metric tons of WEEE were produced in 2012. It was also predicted that the total annual volume would be 33 percent higher, up to 65.4 million tonnes by 2017.<sup>6</sup> The 2012's e-waste generation in countries of the top 10 highest GDP in the same year is depicted in Fig. 1 (b) on the basis of data from the e-waste world map.<sup>7</sup> E-waste contains various kinds of metal, the fraction of which reaches over 60%, including iron, copper, aluminium, gold and many other metals.<sup>5</sup> Many metals in e-waste are recoverable, reusable and recyclable: 20% copper in PCBs (Printed Circuit Boards)<sup>8</sup> and 19-28% PbO in CRT (Cathode Ray Tube) glass.<sup>9</sup> Some of them are very scarce. The

content of gold in cell phones was estimated to be 341g/t.<sup>10</sup> So the emerging terminology, urban mining, was coined (metal in e-waste is the main target of urban mining).<sup>11</sup> Extracting metals from second-hand resources is conceptually and logically similar to mining raw ores. So it is feasible to refer to the methods of extractive metallurgy when extracting metals from e-waste.

Mechanochemistry, as a recently high-profile branch of chemistry (Chem. Soc. Rev. issued the mechanochemistry--themed collection in 2013's September<sup>12</sup>), has been used in the extractive metallurgy for around 300 years.<sup>13</sup> Inspired by the similarity between extractive metallurgy and metal recovery from second-hand resources, many studies on recycling metal via mechanochemistry, such as extracting lead in CRT glass<sup>14</sup>, have been conducted successfully. Due to the emergency of metal sustainability and the feasibility of mechanochemistry, more waste, especially e-waste, should be added onto the ore list for mechanochemistry. This paper reviews the status quo of the application of mechanochemistry to the metal recovery from second-hand resources, analyses the mechanochemical process to enlighten future research and discusses the perspective of mechanochemical research in metal recovery from waste.



**Fig. 1** (a) the 2004-2013 production of five types of EEEs in China; (b) the e-waste generation of 2012 in countries of the top 10 highest GDP in the same year.

## Application oriented mechanochemistry

### Brief introduction of mechanochemistry and its apparatus

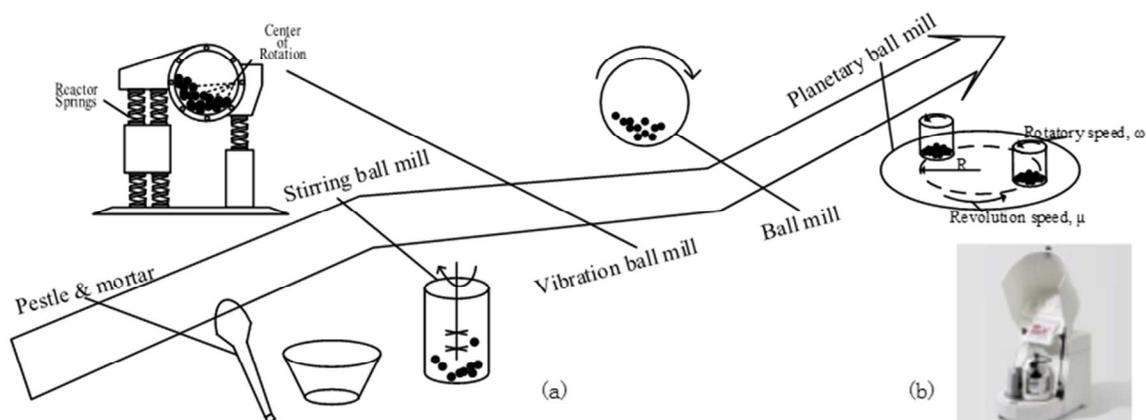
Mechanochemistry means a chemical reaction that is induced by the direct adsorption of mechanical energy (from the IUPAC Compendium of Chemical Terminology).<sup>15</sup> Throughout the history of mechanochemistry, practical applications have always been essential.<sup>13, 16</sup> The earliest documented mechanochemical reaction, milling of cinnabar (as illustrated in Eq. (1)), was done by Theophrastus of Eresus (371-286 BC), student and successor of Aristotle<sup>17</sup>. Matthew Carey Lea (an American chemist, 1823-1897) first founded mechanochemistry as a separate branch of chemistry at the end of the 19th century and found the decomposition of silver and mercuric halides by trituration in a porcelain mortar<sup>18</sup>. In the early stage of its development, mechanochemistry was limited to the field of mineral engineering and focused on countless types of minerals. Later, the gradual recognition of its benefits of time, simplicity,

cost and less waste<sup>19</sup> broadens the mechanochemical applications, such as extractive metallurgy, chemical engineering, building industry, coal industry, materials engineering, agriculture, pharmacy and waste management<sup>16</sup>. It is worth mentioning that mechanochemistry has some successful environmental applications, such as the degradation of persistent organic pollutants (POPs)<sup>20,21</sup>, fly-ash modification<sup>22</sup> and contaminated site remediation<sup>23</sup>.



The apparatus that mechanochemistry depends on plays the core role in whatever mechanochemical research and, also, its development reflects the history of mechanochemistry to some extent. Fig. 2 (a) depicts several important and typical equipments of mechanochemistry. The planetary ball mill has been all the rage in current mechanochemistry research, as shown in Fig. 2 (b).

### Mechanochemistry in extractive metallurgy



**Fig. 2** (a) five important and typical equipments of mechanochemistry (the picture of vibration ball mill refers to the General Kinematics VIBRA-DRUM® grinding mills; the ones of stirring ball mill and ball mill refer to Balaz's book<sup>16</sup>); (b) a planetary ball mill's real image (Planetary Mono Mill PULVERISETTE 6 classic line, FRITSCH, Germany).

Mechanochemical process helps to decompose various minerals, such as tungsten concentrate, molybdenite, monazite, rutile and so forth, and enhances the leaching of targeted metal.<sup>16</sup> Generally, there are two courses of mechanochemical application in extractive metallurgy: milling and leaching as separated processes (dry milling, DM) and simultaneous milling/leaching (wet milling, WM).<sup>16</sup> For example, Maurice<sup>24</sup> mechanically activated a complex ore concentrate containing both pentlandite and chalcopyrite through a horizontal ball mill and then used a concentrated (~5 M Cl<sup>-</sup>) ferric chloride solution for the leaching. It was found that the kinetics both of copper extraction from the chalcopyrite and of nickel extraction from the pentlandite accelerated. Pawlek<sup>25</sup> resorted to the latter course and after mechanochemical process, the copper concentrates (suspended only in water) could be completely dissolved under oxygen over-pressure and temperatures ranging

from 120-180 °C when sodium hydroxide was added. Metal recovery via mechanochemistry can refer to these courses.

### Metal recovery from second-hand resource via mechanochemistry

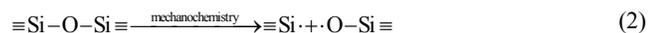
#### Lead recovery from CRT glass and leaded ceramic

The CRT glass, which comprises panel glass, funnel glass and neck glass, is the main component of old-style personal computers or TV sets and the lead in funnel glass reaches about 20 wt%.<sup>26</sup> Sasai<sup>27</sup> developed a novel non-heating method to simultaneously recover both lead and SiO<sub>2</sub> glass matrix from spent lead-glass powder. After the powder was co-milled with water and sodium ethylenediaminetetraacetate (Na<sub>2</sub>EDTA) (one common metal chelate reagent), more than 99% of lead was extracted as a lead-EDTA species from the solid silica glass network matrix. By adding ferric sulfate (Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>·14H<sub>2</sub>O) and continually adjusting pH, 100% lead was recovered as sulfate (PbSO<sub>4</sub>) and 100% iron ions were collected as iron

hydroxide precipitate and, also, Na<sub>2</sub>EDTA was recycled.

Different from Sasai's WT, Yuan took use of DM to recover lead from CRT funnel glass.<sup>14,28</sup> By comparing the pH values in the distilled water leaching before and after ball milling, Yuan confirmed that great changes could happen to the cations surrounding the silica network after mechanochemical process. When diluted in weak nitric acid, the lead leaching ratio of the 500-rpm mechanically activated powder went up to 92.5%. Following the acid leaching was the sulfurization that treated the activated glass sample with sulfur to form lead sulfide, which is the final product. Sasai paid more attention to the optimization of his experiment's parameters and, as a result, both a higher leaching ratio and an integrated process route (as shown in Fig. 3) were presented in Sasai's work. In comparison, more discussions on the mechanism behind mechanical activation were made in Yuan's work, by virtue of as many

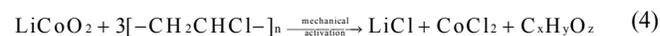
instruments as possible, such as SEM, ESR and XRD. The ESR results indicated scissions of chemical bonds,  $\equiv\text{Si}-\text{O}-\text{Si}\equiv$  and  $\equiv\text{Si}-\text{O}-\text{A}$ , took place to generate  $\text{E}'$  center ( $\equiv\text{Si}\cdot$ ) and non-bridging oxygen hole center (NBOHC) when CRT funnel glass with the framework structure of a  $\text{SiO}_4$  tetrahedron was mechanically activated. Eq. (2) and (3) were provided in Yuan's paper<sup>14</sup>. His further works<sup>29, 30</sup> focused on the sulfuration mentioned above and the development of a complete process route.



Zhang<sup>31</sup> evaluated the efficiency of lead extraction from CRT funnel glass in strong alkaline solution after mechanochemical process and found that the WM was more effective than the DM. More than 97% of Pb in the CRT funnel glass could be extracted with a stirring ball mill leaching process in 5 M sodium hydroxide at 70°C. Kamiya co-milled lead zirconate titanate (PZT) ceramics<sup>32</sup> and PLZT ( $(\text{Pb}_{0.9}\text{La}_{0.1})(\text{Zr}_{0.52}\text{Ti}_{0.48})\text{O}_3$ )<sup>33</sup> with aqueous  $\text{H}_2\text{SO}_4$  solution, respectively, and more than 99 wt% of lead in PZT was recovered as  $\text{PbSO}_4$  by the WM for more than 48h.

### Lithium and Cobalt recovery from lithium-ion batteries

relation between the two processes. Saeki deduced Eq. (4) based on the analysis of solid remains.



Zhang et al.<sup>38</sup> experimented on the real lithium-ion battery scraps, containing  $\text{LiCo}_{0.2}\text{Ni}_{0.8}\text{O}_2$  and polyvinylidene fluoride (PVDF). After milling with some alumina, the amorphization of raw materials could be easily observed and it was easy to extract Co, Ni and Li with dilute nitric acid solution at room temperature. It took 30 minutes' grinding to obtain 100% Li yield, 60 min for over 90% Co and 60 min for 100% Ni. Zhang concluded alumina played a big role in breaking the structure of  $\text{LiCo}_{0.2}\text{Ni}_{0.8}\text{O}_2$  as well as the PVDF binder during the grinding. Fig. 4 is the experiment procedure proposed by Zhang. Lee<sup>39</sup> subjected lithium-ion secondary battery scrap (containing  $\text{LiCoO}_2$ , graphite and PVDF (poly vinylidene fluoride)) to DM using a planetary ball mill with and without quartz powder as a grinding aid and used room temperature leaching in 1M HCl solution. Co and Li in the scrap could be easily extracted from the ground product, and the former yield reached about 90 mass% after 4 hours' grinding with 50 wt% additive.

### Rare earth recovery from fluorescent lamps

Rare earth elements (REEs), which are extensively used in

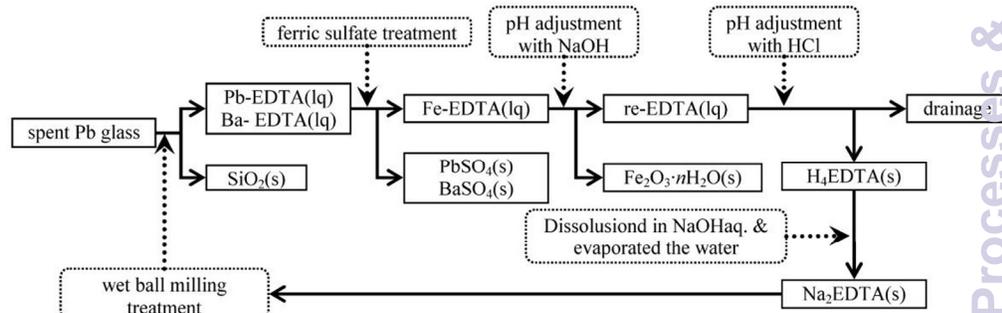
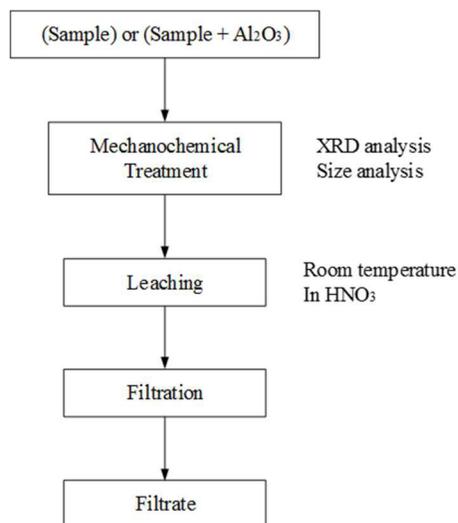


Fig. 3 Schematic diagram of a novel material recycling system for spent lead-glass powder.<sup>45</sup>

Due to its many advantages, e.g. a higher energy density, higher cell voltage, less memory effect, low self-discharge, very good cycle life and environmental soundness, the annual production of the more and more widely-used lithium-ion battery increased by 800% (2000-2010), all over the world<sup>34</sup>.  $\text{LiCoO}_2$ , the main component of cathodes, accounts for 27.5 wt% in a typical lithium-ion battery<sup>35</sup> and recovery of lithium and cobalt is the primary objective in the recycling of spent lithium-ion battery in consideration of both being rare and precious<sup>36</sup>. Saeki et al.<sup>37</sup> co-grinded  $\text{LiCoO}_2$  with PVC (polyvinyl chloride) and both soluble Li of amorphous state and Co-chlorides of a crystal form were detected in the ground product. When the ground product was dispersed in water, Li in amorphous  $\text{LiCoO}_2$  tended to be  $\text{LiOH}$  and Co-chloride was also easily soluble. Through 30 hours' grinding, the Co and Li yields exhibited the highest value (100% and 90%, respectively) and so did the dechlorination ratio of PVC (90%). This implied a close

fluorescent materials, battery alloys and permanent magnet materials in EEES, now encounter a great imbalance between supply and demand<sup>40, 41</sup>. In 2010, REEs' global consumption mounted to 134,000 tonnes in contrast with the production of 133,400 tonnes<sup>42</sup>. The REEs content from fluorescent lamp is about 8,700 g/t, approximately 40 times of natural minerals (150-220 g/t)<sup>42-45</sup>. Zhang<sup>46</sup> based his research of rare earth recovery from waste on his past experience in the hydrometallurgy<sup>47</sup>. The raw material selected was mish metal ( $\text{MmNi}_{3.55}\text{Co}_{0.75}\text{Al}_{0.40}\text{Mn}_{0.30}$ ,  $\text{Mm}=\text{La}_{0.34}\text{Ce}_{0.47}\text{Pr}_{0.04}\text{Nd}_{0.14}$ ), which shared a great similarity with fluorescent lamp phosphor. Zhang co-grinded mish metal with PVC (polyvinyl chloride) and found dechlorination of PVC contributed to the corresponding chlorides' formation of four rare earth elements, but no chlorides formation of nickel and cobalt were observed. After 36 hours' co-grinding, high dechlorination, high chlorides yield and a high-efficiency separating rate between rare earth elements and Ni/Co could be achieved at the same time.

Besides, Zhang<sup>48</sup> extracted the rare earths from fluorescent powder by using 1M HCl solution at room temperature for leaching, after dry grinding of the powder using a planetary ball mill. The dry mechanochemical treatment of the powder caused the structural change of the crystals in the powder into a disordered system and led to easy extraction of the REEs. Only 3 minutes' grinding enabled to extract Y and Eu to above 70-80 % yield. More than 80 % of the other rare earths could be extracted from the powder ground for 2 hours.



**Fig. 4** Synchronized-experiment procedure of decomposing LiCo<sub>0.2</sub>Ni<sub>0.8</sub>O<sub>2</sub> and degrading PVDF proposed by Zhang.<sup>38</sup>

Hattori<sup>49</sup> developed an environmentally friendly process for leaching and effective separation of rare earth elements from waste fluorescent powder. Leaching of fluorescent powder with sulfuric acid at 50°C extracted more than 90% of Y<sup>3+</sup> and Eu<sup>3+</sup>. The mechanochemical treatment with NaOH of the leaching residue of the previous step removed more than 90% of the phosphates of La<sup>3+</sup>, Ce<sup>3+</sup> and Tb<sup>3+</sup>. Each rare earth element was then extracted from the leaching solutions by solvent extraction and precipitation. Todorovsky<sup>50</sup> investigated the influence of mechanochemical process on the overall solubility of phosphogypsum in water and in diluted acids (10% HCl, 7% H<sub>2</sub>SO<sub>4</sub>) as well as on the leaching of rare earths from phosphogypsum. The mechanochemical process was performed in a centrifugal ball mill in air and in suspension with the acids mentioned above. A dissolved fraction, considerably enriched in rare earths (compared to the initial phosphogypsum) was obtained as a result of H<sub>2</sub>SO<sub>4</sub> treatment of the samples activated in water solution.

Much attention was paid to the mill itself in Mio's study of yttrium extraction from fluorescent powder.<sup>51</sup> Mio used a small-scale planetary ball mill to activate red fluorescent powder (Y<sub>2</sub>O<sub>3</sub>) and the yield increased with increasing milling time and rotational speed. Then the Discrete Element Method (DEM) was employed to simulate the three-dimensional motion of each ball during milling and the impact energy of balls could be

calculated, as given in Eq. (5). Here  $V_j$  is the relative velocity between two colliding balls or a ball colliding against the mill wall,  $V_N$  and  $V_T$  are normal component and tangential component respectively,  $m$  is the mass of milling media,  $n$  denotes number of collision within a second and  $W$  is the mass of the sample charged into the mill pot. Mio found that the Y extraction yield and rate were proportional to the specific normal impact energy of balls, irrespective of milling conditions. Further, this relation was applied to estimate the extraction rate using the large-scale mill and designed experiments proved the estimation.

$$E_w = \sum_{j=1}^n \frac{1}{2W} m v_j^2, v_j = \sqrt{v_N^2 + v_T^2} \quad (5)$$

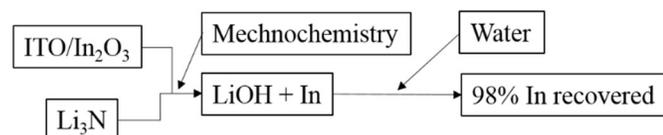
#### Indium recovery from LCD screens

The largest end use of indium is in indium-tin oxide (ITO) thin films, mainly in liquid crystal display (LCD) screens<sup>52</sup> and indium has emerged as an important strategic element in electronic and energy-related industries due to its specific applications and increasing scarcity and demand.<sup>53</sup> Zhang<sup>54</sup> ground the model specimen of indium oxide with tin doping to recover indium. After adding up alumina powder ( $\alpha$ -Al<sub>2</sub>O<sub>3</sub>), the leaching yield exceeded 80%. Murakami et al.<sup>55</sup> followed Zhang's footsteps and investigated the structural explanation behind the change. By grinding with alumina for 15 minutes, sub-nanometric fine particles of indium oxide, which shared the same crystal structure to Zhang's, were produced. When the grinding extended to 30 minutes, the agglomerations of fine particles of indium oxide were observed and, subsequently, the yield decreased. So Murakami concluded that mechanochemical process helped to enlarge the effective surface area that enhanced the indium leaching.

Hasegawa's study<sup>53</sup> focused on the comparison between DM and WT. EDTA and NTA were selected from five aminopolycarboxylate chelants (IDSA, HIDA, NTA, EDTA, DTPA), based on their reactive activity with In<sub>2</sub>O<sub>3</sub> and ITO-glass. The contrast of extraction yields achieved via the chelant washing of a 6 hours' dry milled sample and a wet milled sample at different time intervals (up to 6 hours) indicated the chelant-induced (EDTA or NTA) dissolution of indium from the dry milled sample occurred promptly and, after 60 minute, decelerated proceeding to the equilibrium with time, but a different trend was observed for WT. The high dynamic range (HDR) images of wet-grinded samples looked bigger than dry-grinded ones'. Hasegawa attributed this to the mechanochemical effect as well as the crush extent. No further discussion was given.

Kano<sup>56</sup> proposed a non-thermal process of milling indium(III) oxide (In<sub>2</sub>O<sub>3</sub>) and/or indium tin oxide (ITO) with lithium nitride (Li<sub>3</sub>N) for indium recovery, under (NH<sub>3</sub>) or nitrogen (N<sub>2</sub>) gas environment, as shown in Fig 5. Milling operation caused mechanochemical reaction in the systems of In<sub>2</sub>O<sub>3</sub>/ITO and Li<sub>3</sub>N, to form In and LiOH. The latter is soluble in water, so

that the milled sample was subjected to washing with water, enabling to recover indium-metal. As a result, the yield of In from the starting oxide sample was more than 97% and this process could be applied to recover indium-metal from electric device wastes containing ITO. Lee<sup>57</sup> first crushed ITO glass to micron size particles in seconds via high energy ball milling (HEBM) and leached the particles in the HCl acid solution. The results showed that by crushing ITO glass to micron size particles by HEBM, it was possible to extract higher amount (86%) of indium at room temperature than that by conventional methods using only conventional shredding machines.



**Fig. 5** The experimental route of In recovery by Kano<sup>56</sup>.

### Cooper recovery from waste printed circuit boards

Waste printed circuit boards (WPCBs) seem the most common type of e-waste as printed circuit boards are the essential part of almost all EEEs<sup>58</sup>. WPCBs contain a large amount of metals (~40%)<sup>58</sup>: copper (the largest ratio), alumina, lead, zinc, nickel, iron, tin, antimony, chromium, molybdenum, aurum, platinum, silver, palladium, etc. The averaged content of copper reaches 17.6% (5.8~26.8% for different sources)<sup>58</sup> while typical copper ores contain from 0.5% Cu (open pit mines) to 1 or 2% Cu (underground pit mines).<sup>59</sup> Ou<sup>60</sup> verified that copper and sulfur could form into copper sulfide by the aid of mechanochemistry in the model experiment. Based on this, the synergistic route of mechanical activation and sulfurization was proposed. The model experiment, where copper and sulfur were mixed and ground, not only verified the feasibility of this route, but also determined the optimal ball milling time (20 minutes). In the practical experiment, WPCB fragments and sulfur were mixed and ground for 20 minutes, no copper was detected but copper sulfide was left. After leaching in sulfuric acid (3M) and hydrogen peroxide (30 wt%), the yield of copper reached nearly 90% and, also, resin was conserved for further utilization.

### Au, Mo and Ni recovery from waste

Ficeriová<sup>61</sup> enhanced the gold leaching from a gold-containing waste using WM (in water and in thiourea solution) as the pre-treatment steps. The leaching of the sample in an acid thiourea solution resulted in 78 % Au dissolution. After leaching again, up to 99 % of the gold was extracted during 120 min. The mechanochemical process resulted in an increase of the specific surface area of the waste from 0.6 m<sup>2</sup>g<sup>-1</sup> to a maximum value of 20.5 m<sup>2</sup>g<sup>-1</sup>. The activation was performed in an attritor using variable milling times. The physico-chemical changes in the waste as a consequence of mechanochemistry had a pronounced influence on the subsequent gold extraction.

Ferella<sup>62</sup> focused on physico-mechanical pre-treatments of spent hydro-treating catalysts aimed at concentration of at least one of the valuable metals contained in such secondary raw material. In particular, dry Ni-Mo and Co-Mo as well as wet Ni-Mo catalysts were used. Flotation, grain size separation and attrition processes were tested. After that, a rods vibrating mill and a ball mill were used to ground the catalysts in order to understand the best mechanical pre-treatment before leaching extraction. The results showed that flotation is not able to concentrate any metals due to the presence of coke or other depressant compounds. The particle size separation produces two fractions enriched in Mo and Co when dry Co-Mo catalyst was used, whereas attrition was not suitable as metals are uniformly distributed in rings' volume. Roasting at 550°C and vibrating grinding were the most suitable pre-treatments conditions that were able to produce fractions easily leached by NaOH and H<sub>2</sub>SO<sub>4</sub> after grain size separation.

### Discussion and conclusion

As reviewed above, mechanochemistry has been successfully applied to recover a wide variety of metals, including indium, lead, REEs, gold, copper, lithium, cobalt, molybdenum and nickel. Table 1 gives a summary on the current studies that applied mechanochemical process to metal recovery from second-hand resources and attempts to conclude some patterns of mechanochemical application in metal recovery.

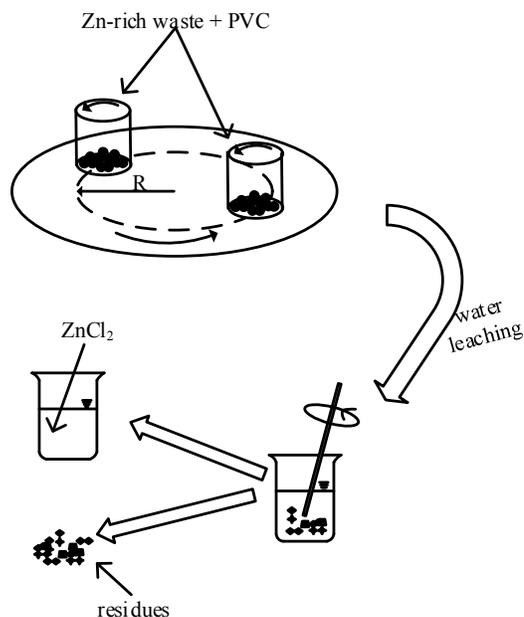
Generally, the current applications can be divided to two types

**Table 1.** Summary of all the specific types of milling in current metal recovery from e-waste.

| Metal   | Waste                     | Type of mill  | Milling method                           | Yield                  | Leaching condition                                    | Ref.      |
|---------|---------------------------|---------------|--|------------------------|---|-----------|
| Pb      | CRT funnel glass          | planetary     | DM                                       | 92.5%                  | 3 M HNO <sub>3</sub> , 95 °C, 1h, L:S=150             | 14, 28-30 |
|         | spent lead-glass powder   | planetary     | WM, +Na <sub>2</sub> EDTA                | >99%                   | -   | 27        |
|         | CRT funnel glass          | stirring mill | DM                                       | ≈40%                   | 5M NaOH, 70°C, 2h                                     | 31        |
|         | PZT ceramic               | pot mill      | WM, 4.5 M H <sub>2</sub> SO <sub>4</sub> | 99.9%                  | -   | 32        |
|         | PLZT ceramic              | apparatus     | WM, 4.5 M H <sub>2</sub> SO <sub>4</sub> | 99%                    | -   | 33        |
| Li & Co | lithium-ion battery scrap | planetary     | DM, +quartz powder                       | Co>90%, Li 100%        | 1M HCl, ambient temperature, 2h, L:S=100              | 39        |
|         | lithium-ion battery scrap | planetary     | DM, +PVDF/quartz powder                  | Li100%, Co>90%, Ni100% | Dilute HNO <sub>3</sub> , ambient temperature         | 38        |
|         | LiO <sub>2</sub> powder   | planetary     | DM                                       | Li 60%                 | Water, ambient temperature, 1h,                       | 46        |
|         |                           | planetary     | DM, +PVC                                 | Co >90%, Li 100%       | L:S=250   | 37        |
| REEs    | mis metal                 | planetary     | DM, +PVC                                 | high                   | This journal is © The Royal Society of Chemistry 2016 | 46        |
|         | phosphogypsum waste       | planetary     | WM, +water                               | (La, Ce, Pr, Nd) 70%   | 7% H <sub>2</sub> SO <sub>4</sub> , L:S=5             | 50        |
|         |                           |               |  | Y 100%, (Eu, La,       | 1M HCl, ambient temperature,                          |           |

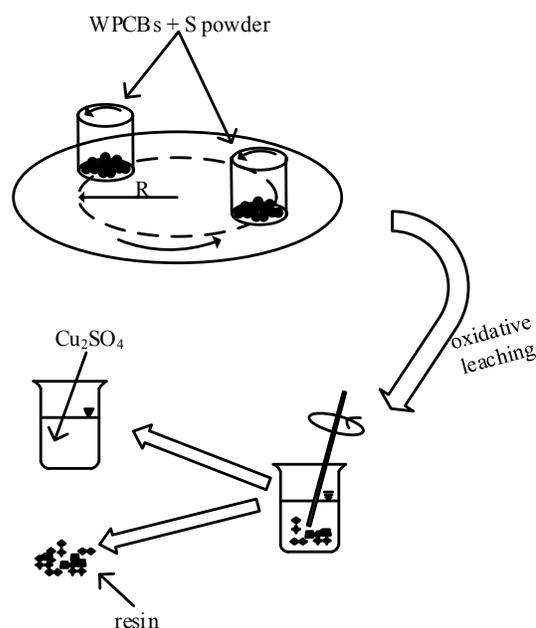
of milling, the WT and the DM, which just follow the types in extractive metallurgy. The biggest difference between the two lies in the combination or separation of ball milling and leaching. Ball milling contributes to the structural breakage which makes it easier for the leachant to extract metal. For instance, the decomposition of crystal structure of CRT glass after DM raised the Pb leaching yield from negligible 1.2-2.8% to a high of 92%.<sup>14</sup> The WT integrates mechanochemical process and leaching into one step, where the targeted metal dissolves into liquid phase during ball milling. Liquid are often selected from acid, water or chelate reagents. Ball milling leads to bond breakage and thus promotes chemical reactions, which result in the formation of the corresponding metal compounds so that enhanced leaching or dissolving can be fulfilled. Lead recovery from PZT and PLZT ceramics did follow this route.<sup>32</sup>  
<sup>33</sup> Also, the reduction of particle size and the rise of specific surface area enhance the metal leaching with the ball milling. In Ou's paper<sup>60</sup>, the average particle size dropped to around 10  $\mu\text{m}$  after 20 minutes' milling. These physical and chemical changes help to decrease activation energy in order to make metal extraction easier.

Except the additive liquid in WT, it is an effective method to add up grinding aids. Some grinding aids purely enhance the milling efficiency, such as  $\text{Al}_2\text{O}_3$  and quartz. Some others participate in solid-solid reaction that makes the following leaching easier or more efficient. It was confirmed that Li and Co could be transformed to easily leachable  $\text{LiCl}$  and  $\text{CoCl}_2$  by co-milling  $\text{LiCoO}_2$  in batteries with PVC. These innovated dry-milling methods give a reference when it comes to recovery method option in the future. Xiao's work<sup>63</sup> verified that zinc can be chlorinated by co-milling with PVC. So possible Zn recovery can be done as shown in Fig. 6. Water is used as the leachant after co-milling Zn-rich waste with PVC, and  $\text{ZnCl}_2$  is much leachable. The process not only achieves both Zn recovery and PVC degradation, but also never involves acid which is commonly employed so that it seems more sustainable.



**Fig. 6** Possible schematic route of Zn recovery from Zn-rich waste.

Ou's work<sup>60</sup> provides another interesting alternative route. Second-hand resource is like synthetic materials, not natural minerals, so that there exists great difference between the states of metal being present in second-hand resources and in natural minerals. It is not easy to take direct use of traditional methods in mineral extractive processing to deal with them. If it is difficult to directly leach the targeted metal from scraps, it seems an alternative method to transform the targeted metal into its corresponding compound that exists in natural minerals and, then, methods in traditional mineral engineering can be taken into use. Mechanochemistry helps to achieve this transform. As shown in Fig 7, WPCB was co-milled with sulfur



powder to obtain copper sulfides which is the most commonly present copper minerals in the crust. Then the oxidative leaching (dilute sulfuric acid and peroxide hydrogen) was taken use of to finally get a high copper leaching yield. This route was environmentally-friendly because it avoided strong acid involvement which is commonly used in copper extraction. This pathway is based on the similarity between mechanochemical process and geochemical one in metal sulfurization. So this pathway can be generalized to some other metal, e.g. lead, that is commonly present as corresponding sulfides in nature. Yuan's work<sup>14</sup> actually followed the analogous route. Yuan did not directly aim at enhanced leaching. After DM, Yuan mixed sulfur with activated powder to easily get PbS, which is the main component in galena. And in mining industry lead separation from galena has been well studied. Such thinking was also embodied in Wang's research<sup>64</sup>, where two kinds of waste containing nonferrous metals (in oxide or metal) and iron/aluminium metals were ground with sulfur sample. The products, including nonferrous metal sulfides and iron/aluminium oxides, appealed to the well-developed mineral processing technologies.

#### Fig. 7 Copper recovery from WPCBs via mechanochemistry.

What is worth mentioning is the mechanochemical apparatus because mechanochemical research totally depends on it. The planetary ball mill is the most often used apparatus in these studies, which can provide a high energy density, producing high mechanical and mechanochemical activation in a relatively short milling time.<sup>65</sup> The attritor and the stirring mill are also involved in some studies. However, proper milling apparatus that can generate sufficient rotational speed (representing impact energy) for industrial applications should be developed, in view of the need of high efficiency.

In the near future, mechanochemistry will be probably embracing a rapid development and prosperity. It is a reasonable inference that more researches on applications of mechanochemistry to the metal recovery from second-hand resources will be done. However, current mechanochemical application in metal recovery is still limited on the laboratory scale. The scalability of mechanochemical method need to be paid more attention, as well as the balance between energy consumption and productivity. After that, wide use of mechanochemistry in metal recycling can be expected in term of its environmental and economic benefits.

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#### Notes and references

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- R. M. Izatt, S. R. Izatt, R. L. Bruening, N. E. Izatta and B. A. Moyer, *CHEM SOC REV*, 2014, **43**, 2451-2475.
- O. A. Ogunseitan, J. M. Schoenung, J. M. Saphores and A. A. Shapiro, *SCIENCE*, 2009, **326**, 670-671.
- I. K. Wernick and N. J. Themelis, *Annu. Rev. Energ. Env.*, 1998, **23**, 465-497.
- T. E. Graedal, *Recycling Rates of Metals-a Status Report, a Report of the Working Group On the Global Metal Flows to Unep's International Resource Panel*; [http://www.unep.org/resourcepanel/portals/24102/pdfs/UNEP\\_report2\\_Recycling\\_130920.pdf](http://www.unep.org/resourcepanel/portals/24102/pdfs/UNEP_report2_Recycling_130920.pdf), accessed: July, 2014.
- R. Widmer, H. Oswald-Krapf, D. Sinha-Khetriwal, M. Schnellmann and H. Böni, *Environmental Impact Assessment Review*, 2005, **25**, 436-458.
- K. Takeuchi, J. Nishida, J. Linnell and J. Clark, *World E-Waste Map Reveals National Volumes, International Flow*; <http://i.unu.edu/media/unu.edu/news/41225/World-E-Waste-Map-Reveals-National-Volumes-International-Flows.pdf>, accessed: StEP, 2013.
- E. L. Sum, *JOM-US*, 1991, **43**, 53-61.
- ICER, *Materials Recovery From Waste Cathode Ray Tubes (CRTs)*; [http://www.glass-ts.com/userfiles/files/2004%20-%20WRAP%20-%20Materials%20recovery%20from%20waste%20cathode%20ray%20tubes%20\(CRTs\).pdf](http://www.glass-ts.com/userfiles/files/2004%20-%20WRAP%20-%20Materials%20recovery%20from%20waste%20cathode%20ray%20tubes%20(CRTs).pdf), accessed: March.
- C. Hagelucken and C. E. M. Mesker, in *Electronic Goes Green 2008+*, Berlin, Germany, 2008, pp. 623-628.
- R. Cossu, V. Salieri and V. Bisinella, *Urban Mining: A Global Cycle Approach to Resource Recovery From Solid Waste*, CISA, Padova, Italy, 2012.
- R. Eagling and J. Hordern, *CHEM SOC REV*, 2013, **42**, 7489-7493.
- L. Takacs, *CHEM SOC REV*, 2013, **42**, 7649-7659.
- W. Yuan, J. Li, Q. Zhang and F. Saito, *ENVIRON SCI TECHNOL*, 2012, **46**, 4109-4114.
- A. D. McNaught and A. Wilkinson, *Iupac. Compendium of Chemical Terminology, 2Nd Ed. (The "Gold Book")*, Blackwell Scientific Publications, Oxford, 1997.
- P. Balaz, *Mechanochemistry in Nanoscience and Minerals Engineering*, Springer, Verlag Berlin Heidelberg, 2008.
- P. Balaz, M. Achimovicova, M. Balaz, P. Billik, Z. Cherkezova-Zheleva, J. M. Criado, F. Delogu, E. Dutkova, E. Gaffet, F. J. Gotor, R. Kumar, I. Mitov, T. Rojac, M. Senna, A. Streletskii and K. Wiczorek-Ciurova, *CHEM SOC REV*, 2013, **42**, 7571-7637.
- L. Takacs, *J MATER SCI*, 2004, **39**, 4987-4993.
- S. L. James and T. Friscic, *CHEM COMMUN*, 2013, **49**, 5349-5350.
- S. Loisel, M. Branca, G. Mulas and G. Cocco, *ENVIRON SCI TECHNOL*, 1997, **31**, 261-265.
- A. K. Hall, J. M. Harrowfield, R. J. Hart and P. G. McCormick, *ENVIRON SCI TECHNOL*, 1996, **30**, 3401-3407.
- J. H. Yan, Z. Peng, S. Y. Lu, X. D. Li, M. J. Ni, K. F. Cen and H. F. Dai, *J HAZARD MATER*, 2007, **147**, 652-657.
- A. Nasser and U. Mingelgrin, *APPL CLAY SCI*, 2012, **67-68**, 141-150.
- D. Maurice and J. A. Hawk, *HYDROMETALLURGY*, 1998, **49**, 103-123.
- F. E. Pawlek, *The Metallurgical Society Of AIME*, Warrendale, PA, USA, 1976, pp. 690-705.
- F. Méar, P. Yot, M. Cambon and M. Ribes, *WASTE MANAGE*, 2006, **26**, 1468-1476.

- 1 27 R. Sasai, H. Kubo, M. Kamiya and H. Itoh, *ENVIRON SCI* 64 J. Wang, J. Lu, Q. Zhang and F. Saito, *IND ENG CHEM RES*,  
2 *TECHNOL*, 2008, **42**, 4159-4164. 2003, **42**, 5813-5818.
- 3 28 W. Yuan, J. Li, Q. Zhang, F. Saito and B. Yang, *J AIR WASTE* 65 E. L. Fokina, N. I. Budim, V. G. Kochnev and G. G. Chernik, *J*  
4 *MANAGE*, 2013, **63**, 2-10. *MATER SCI*, 2004, **39**, 5217-5221.
- 5 29 W. Yuan, J. Li, Q. Zhang, F. Saito and B. Yang, *J AIR WASTE*  
6 *MANAGE*, 2013, **63**, 418-423.  
7 30 W. Yuan, J. Li, Q. Zhang and F. Saito, *POWDER TECHNOL*,  
8 2012, **230**, 63-66.  
9 31 C. Zhang, J. Wang, J. Bai, J. Guan, W. Wu and C. Guo, *WASTE*  
10 *MANAGE RES*, 2013, **31**, 759-763.  
11 32 M. Kamiya, R. Sasai and H. Itoh, *J CERAM SOC JPN*, 2003, **111**,  
12 806-810.  
13 33 M. Kamiya, R. Sasai and H. Itoh, *J CERAM SOC JPN*, 2003, **111**,  
14 897-901.  
15 34 X. Zeng, J. Li and N. Singh, *CRIT REV ENV SCI TEC*, 2013, **44**,  
16 1129-1165.  
17 35 C. K. Lee and K. Rhee, *J POWER SOURCES*, 2002, **109**, 17-21.  
18 36 J. Xu, H. R. Thomas, R. W. Francis, K. R. Lum, J. Wang and B.  
19 Liang, *J POWER SOURCES*, 2008, **177**, 512-527.  
20 37 S. Saeki, J. Lee, Q. Zhang and F. Saito, *INT J MINER PROCESS*,  
21 2004, **74**, Supplement, S373-S378.  
22 38 Q. Zhang, J. Lu, F. Saito, C. Nagata and Y. Ito, *ADV POWDER*  
23 *TECHNOL*, 2000, **11**, 353-359.  
24 39 J. Lee, Q. Zhang and F. Saito, *Shigen-to-Sozai*, 2000, **116**, 919-  
25 922.  
26 40 K. Binnemans, P. T. Jones, B. Blanpain, T. Van Gerven, Y. X.  
27 Yang, A. Walton and M. Buchert, *J CLEAN PROD*, 2013, **51**, 1-  
28 22.  
29 41 Q. Tan, J. Li and X. Zeng, *CRIT REV ENV SCI TEC*, in press.  
30 42 J. Gambogi and D. J. Cordier, *Rare Earths, in Metals and*  
31 *Minerals: U.S. Geological Survey Minerals Yearbook 2010*;  
32 [http://minerals.usgs.gov/minerals/pubs/commodity/rare\\_earths/my](http://minerals.usgs.gov/minerals/pubs/commodity/rare_earths/myb1-2010-raree.pdf)  
33 [b1-2010-raree.pdf](http://minerals.usgs.gov/minerals/pubs/commodity/rare_earths/myb1-2010-raree.pdf), accessed:  
34 43 F. Yang, F. Kubota, Y. Baba, N. Kamiya and M. Goto, *J*  
35 *HAZARD MATER*, 2013, **254 - 255**, 79-88.  
36 44 L. Meyer and B. Bras, in *2011 IEEE International Symposium on*  
37 *Sustainable Systems and Technology (ISSST)*, Chicago, IL, 2011,  
38 pp. 1-6.  
39 45 M. A. Rabah, *WASTE MANAGE*, 2008, **28**, 318-325.  
40 46 Q. Zhang, S. Saeki, Y. Tanaka, J. Kano and F. Saito, *J HAZARD*  
41 *MATER*, 2007, **139**, 438-442.  
42 47 Q. W. Zhang and F. Saito, *HYDROMETALLURGY*, 1998, **47**,  
43 231-241.  
44 48 Q. Zhang and F. Saito, *Shigen-to-Sozai*, 1998, **114**, 253-257.  
45 49 S. Hattori, N. Murayama and J. Shibata, *KAGAKU KOGAKU*  
46 *RONBUN*, 2013, **39**, 472-478.  
47 50 D. Todorovsky, A. Terziev and M. Milanova,  
48 *HYDROMETALLURGY*, 1997, **45**, 13-19.  
49 51 H. Mio, J. Y. Lee, T. Nakagawa, J. Kano and F. Saito, *MATER*  
50 *TRANS*, 2001, **42**, 2460-2464.  
51 52 A. M. Alfantazi and R. R. Moskalyk, *MINER ENG*, 2003, **16**,  
52 687-694.  
53 53 H. Hasegawa, I. Rahman, Y. Egawa, H. Sawai, Z. A. Begum, T.  
54 Maki and S. Mizutani, *MICROCHEM J*, 2013, **106**, 289-294.  
55 54 Q. Zhang, T. Aoyagi, C. Nagata and F. Saito, *Journal of MMIJ*,  
56 1999, **115**, 185-188.  
57 55 Y. Murakami, D. Shindo, Q. Zhang and F. Saito, *Materials*  
58 *Science and Engineering: A*, 2002, **332**, 64-69.  
59 56 J. Kano, E. Kobayashi, W. Tongamp, S. Miyagi and F. Saito, *J*  
60 *ALLOY COMPD*, 2009, **484**, 422-425.  
61 57 C. Lee, M. Jeong, M. Fatih Kilicaslan, J. Lee, H. Hong and S.  
62 Hong, *WASTE MANAGE*, 2013, **33**, 730-734.  
63 58 H. B. Duan, K. Hou, J. H. Li and X. D. Zhu, *J ENVIRON*  
64 *MANAGE*, 2011, **92**, 392-399.  
65 59 S. Mark, K. Matthew, S. Kathryn and D. William, *Extractive*  
66 *Metallurgy of Copper*, Elsevier, 2011.  
67 60 Z. Ou and J. Li, *RSC ADV*, 2014, **4**, 51970-51976.  
68 61 J. Ficeriova and P. Balaz, *ACTA MONTAN SLOVACA*, 2010.  
69 62 F. Ferella, A. Ognyanova, I. De Michelis, G. Taglieri and F.  
70 Vegliò, *J HAZARD MATER*, 2011, **192**, 176-185.  
71 63 X. Xiao, Z. Zeng and S. Mao, *J HAZARD MATER*, 2008, **151**,  
72 118-124.