ORIGINAL PAPER

Efficient and low-energy mechanochemical extraction of lead from dumped crystal glass waste

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Abstract

Glass waste dumps from crystal glass production is an health issue due to the occurrence of antimony, arsenic, cadmium and lead in crystal glass. Recovery of those elements could both decrease pollution and recycle metals in the circular economy. Pyrometallurgy is a potential recovery method, yet limited by high energy consumption. Here we tested a lower-energy alternative in which glass is mechanically activated in a ball mill and leached with nitric acid. Results show that mechanical activation destabilised the glass structure and resulted in 78% lead extraction during leaching at 95 °C. Temperature had the most significant effect on extraction, whereas acid concentration, from 0.5 to 3 M, and leaching time, from 0.5 to 12 h, had insignificant effects. In each experiment, 75% of the final extracted amount was achieved within 30 min. The study demonstrates potential for lead extraction from glass waste at lower acid concentration, shorter leaching time and lower temperature, of 95 °C, than traditional pyrometallurgical extraction, typically operating at 1100 °C.

Introduction

Glassworks have been sources of anthropogenic pollutants around the world (Brião et al. 2020; Mutafela et al. 2020a; Rossini et al. 2010). Elements used in crystal glass, such as arsenic (As), cadmium (Cd), antimony (Sb) and lead (Pb) end up in the environment through emissions, effluents and other factory wastes (Mutafela et al. 2020b). They can contaminate soil, surface and ground water, and pose human health hazards (Keng et al. 2014; Malik et al. 2019). In Sweden, contaminated glass dumps are excavated and materials landfilled as a remediation measure. Unlike transferring the contamination problem (Pasalari et al. 2019), remediation could incorporate recovery of the contaminants like Pb for use in batteries, radiation shielding and other protective coatings (Mutafela et al. 2019; Yu et al. 2016).

The only documented method of Pb recovery from crystal glass waste is pyrometallurgy through reduction-melting (Jani and Hogland, 2017), an energy-intensive (1100 °C) process that also emits Pb-containing particulates (Li et al. 2019). Thus, an alternative process is needed to lower the energy footprint and eliminate such emissions. The mechanochemical process, a potential alternative, combines mechanical activation of the glass with hydrometallurgy in Pb extraction (Sasai et al. 2008). Although glass is structurally too stable for ordinary leaching methods to fully liberate elements from its matrix, mechanical activation can destabilise its structure for easy dissolution of Pb ions during leaching (Singh et al. 2016).

The current study, therefore, focuses on the potential for lower-energy extraction of Pb from crystal glass waste through mechanical activation and leaching with nitric acid (HNO_3). Recovery potential was investigated at different leaching temperatures, times and varying acid concentrations. Some activated glass samples were water-leached and lead sulphide (PbS) formation from the leached Pb was assessed.

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Materials and methods

Sampling and mechanical activation of samples

The crystal glass sample investigated was obtained from Madesjö glass waste dump in Nybro, southeastern Sweden. The sample was crushed to smaller pieces, pulverised in a ball mill and sieved to < 125 μm samples, herein referred to as milled glass. The milled sample was then oven-dried at 105 °C for 24 h. Forty grams of the sample was mechanically activated in a 250 ml agate jar of a planetary ball mill with 10 agate balls of 15 mm diameter. The activation was done for 180 min at 500 rpm, after which the activated glass sample was oven-dried at 105 °C for 24 h.

Metal extraction process and lead sulphide formation

Some samples were treated by acid leaching and others by water leaching and sulphidation using a thermostatically controlled shaking water bath (Grant OLS200) at constant solid to liquid ratio. For water leaching, 2 g each of milled and activated glass sample was agitated in 40 ml deionized water at room temperature for 150 min to assess the change in metal availability caused by the mechanical activation process. To generate PbS, another 2 g of activated glass sample was similarly agitated with 0.15 g of analytical grade elemental Sulphur, but at 70 °C, 95 °C and 120 °C (in an autoclave), respectively. After each run, the contents were separated by vacuum filtration.

Acid leaching was carried out at 25 °C, 70 °C and 95 °C in each acid concentration of 0.5 M, 1 M and 3 M HNO_3, respectively. In each case, 2 g of activated sample was agitated with 500 mL HNO_3 in 1 L flasks for 12 h. During the leaching process, 10 mL samples were collected from the flasks at five time points (0.5 h, 1 h, 2 h, 6 h and 12 h) and centrifuged immediately after leaching, before metal content analyses. Pb extraction efficiency was expressed in terms of metal recovery (%) as follows (Wuana et al. 2010):

$$\text{Metal recovery (\%)} = \frac{C_1 V_1}{C_s m_s} \times 100 \tag{1}$$

where C_1 and C_s are the metal concentrations in supernatant (mg L^{-1}) and glass (mg kg^{-1}) respectively; V_1 is the volume of supernatant (L) and m_s is the dry mass of the glass (kg) samples.

Sample characterisation and metal analyses

The milled glass sample was analysed for elemental composition, whereas both milled and activated samples were analysed for morphology, specific surface area, particle size, pore size distribution and volume. In addition, filtration residues from the sulphidation process were analysed for phase identification (PbS peaks) and surface charge, whereas the supernatant (C_1 in Eq. 1) from the acid leaching and sulphidation processes were analysed for metal contents (discussed further in Supplementary Material).

Experimental design and statistical analyses

The effects of leaching temperature, time and acid concentration on Pb extraction were studied based on factorial design of experiments (Montgomery. 2001) and according to the following polynomial equation:

$$R = a0 + a1 \times C + a2 \times T + a3 \times Ti + a4 \times C \times T \times Ti \\ + a5 \times C^2 + a6 \times T^2 + a7 \times Ti^2 \tag{2}$$

where R is the extraction efficiency (%), $a(0–6)$ are the model constants, C is the acid concentration in moles (M), T is the temperature in degrees Celsius (°C) and Ti is the time in seconds. STATISTICA version 6 was used to determine the predicted recovery results and the polynomial equation constants based on the Least Square method.

Results and discussion

Composition of elements in the glass sample

Elemental composition of the milled glass sample was determined as shown in Table 1. According to Swedish limits

Table 1 Composition of elements in the crystal glass sample scanned by X-ray fluorescence. Based on Swedish limits for hazardous waste (Elert et al. 2019), some elements are in hazardous concentrations

Element	Concentration (mg kg^{-1})	Swedish Limits (mg kg^{-1})
As	16,226	1000
Cd	2624	1000
Co	50	1000
Cr	43	1000
Cu	<LOD	2500
Mn	85	
Mo	<LOD	10,000
Ni	1218	1000
Pb	415,576	2500
Sb	10,224	10,000
Si	539,141	
Zn	476	2500

LOD limit of detection

for hazardous waste (Elert et al. 2019), the elements As, Cd, Ni, Pb and Sb were in hazardous concentrations while Cr, Co, Cu, Mo and Zn were lower than their respective hazardous waste limits. The limits of Si and Mn were not stated. The element of interest (Pb) constituted 41.6% of the total elemental concentration in the sample. Concentration of each element corresponded with its use in crystal glass production (Mutafela et al. 2020b).

Characteristics of the milled and activated glass samples

Initial glass milling and sieving through a 125 μm sieve produced varying particles sizes with sharp edges as shown in Fig. 1a. Mechanical activation reduced the particle sizes further, ranging between 200 and 500 nm with agglomeration (Fig. 1b). This conforms with particle sizes evaluated by dynamic light scattering method in Fig. 1c indicating primary particles between 200 and 300 nm and secondary agglomerates around 960 ± 270 nm. Mechanical activation altered glass physical properties to enhance the leaching process, as further discussed in the Supplementary Material.
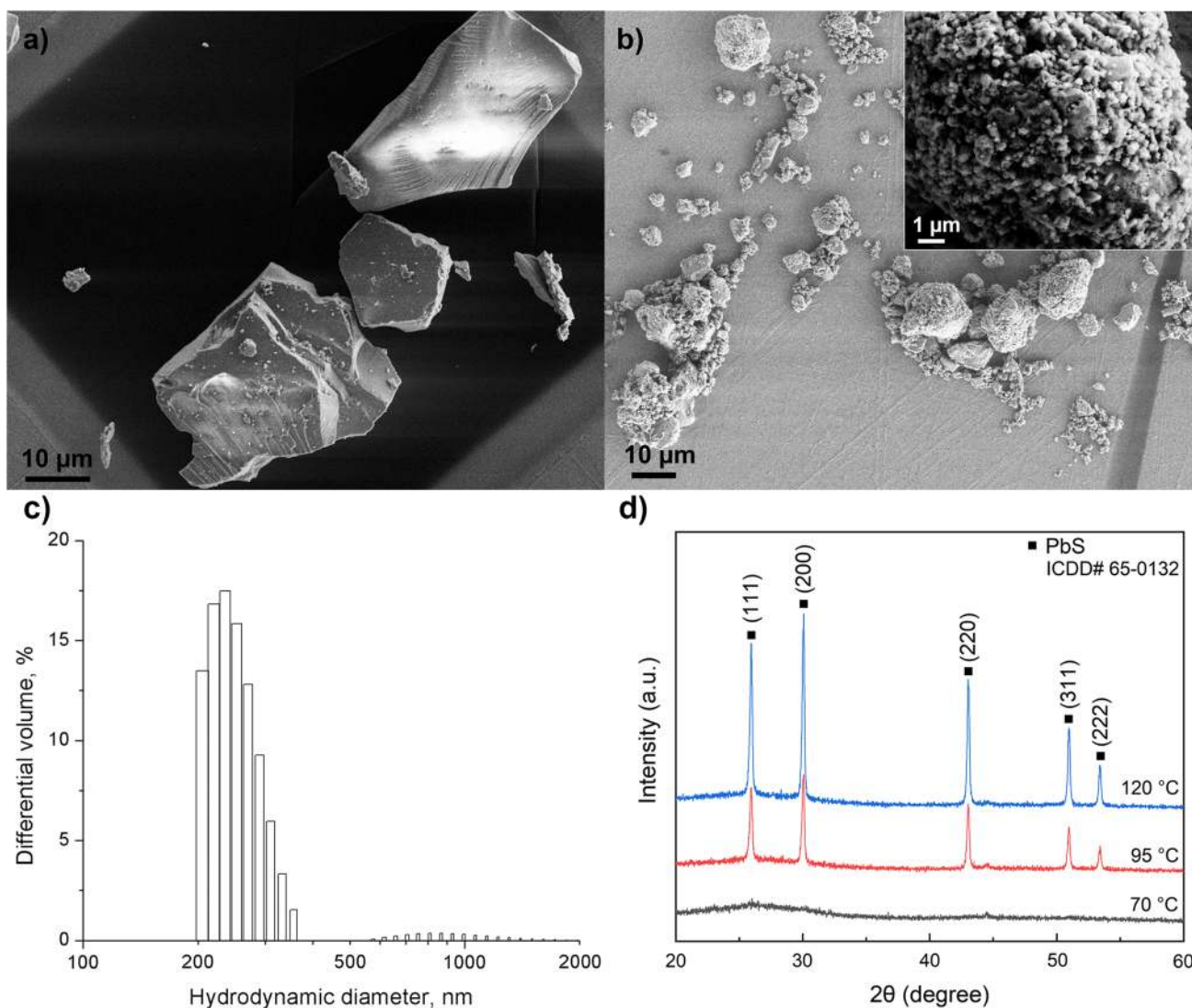

Fig. 1 Scanning electron microscopy images of **a** milled sample and **b** mechanically activated sample with inset showing details of one area with higher magnification; **c** volume-weighted hydrodynamic size distribution of aqueous dispersion of activated glass sample. The size between 200 and 300 nm correlates well with the size obtained from scanning electron microscope imaging; **d** powder X-ray diffraction patterns of the PbS formed at 70 °C, 95 °C and 120 °C. Amorphous phase was obtained at 70 °C, while highly pure crystalline PbS was obtained at 95 °C and 120 °C

Sulphidation process

The potential for PbS generation from leached Pb was assessed at different temperatures to determine the most suitable temperature for crystallization. In Fig. 1d, the PbS obtained at 70 °C only had a broad peak between 25° and 30°, suggesting its amorphous nature. For 95 °C and 120 °C treatments, sharp peaks were observed at 25.9°, 30.0°, 43.0°, 51.0° and 53.4°, which can be indexed to crystal planes of (111), (200), (220), (311) and (222), respectively, according to the International Centre for Diffraction Data (ICDD) Card No.65-0132 (Chongad et al. 2016). Apart from PbS, no other crystalline phases were observed, implying higher purity of the PbS generated at 95 °C and 120 °C. Using the Scherrer equation, the average crystalline sizes of PbS nanoparticles were determined from the highest intensity diffraction peak ((200) plane) as 37.4 nm and 38.4 nm for 95 °C and 120 °C, respectively. Higher temperature generated slightly bigger grain sizes due to faster crystal growth rate. Effects of temperature on PbS generation are discussed further in Supplementary Material.

Metal extraction

The effect of concentration on extraction is shown as a plot of kinetics of each acid concentration at 25 °C, 70 °C and 95 °C in Fig. 2a–c, respectively. The effect of temperature on

leaching kinetics is shown in Fig. 2d. In this study, the kinetics was described based on chemical reaction control and film diffusion control, according to the two-phase exponential association model (Eq. 3) provided by OriginLab (2020):

$$y = y_0 + A_1\left(1 - e^{-x/t_1}\right) + A_2\left(1 - e^{-x/t_2}\right) \tag{3}$$

The model generated fitting curves (dashed lines) shown in Fig. 2a–c, and model parameters (R^2 and rate constants; t_1 and t_2 for the fast and slow steps, respectively) as shown in Table S1 (Supplementary Material). In the modelling based on Eq. 3, a straight line and zero point intercept were obtained for the first 30 min of the extraction process, indicating that the kinetics is controlled by the chemical reaction step at the particle surface (Sancho et al. 2009). The chemical reaction controlling step is expected due to the smaller particle sizes and increased surface area, whereby enough Pb ions are exposed and made readily available by the mechanical activation process, hence the rapid leaching in the first 30 min. As the process proceeds beyond 30 min, the available Pb ions on the particle surface are almost completely leached, and thus, diffusion through the glass particle layer dominates. The amorphous nature of the particles enables Pb ions to diffuse out of the solid phase into the liquid phase during the film diffusion control step. However, Pb ions at this stage are more closely bound to the solid phase than in the previous stage, hence the extraction rate slows down.

Fig. 2 Effect of acid concentration **a–c** and temperature **d** on Pb extraction. The differences in extraction due to acid concentration were not significant for all temperatures. The leaching kinetics increased with temperature and the highest Pb extraction (78%) was achieved by 3 M HNO_3 at 95 °C after 12 h of leaching
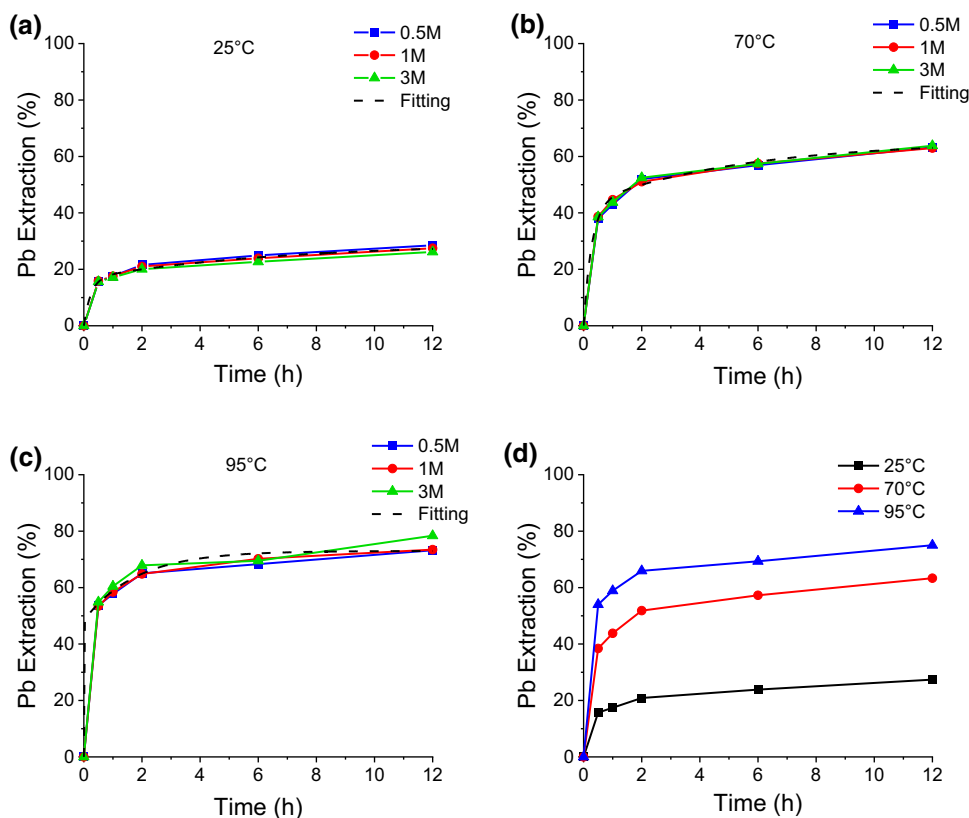
Fig. 3 Comparison between experimental (observed) and theoretical (predicted) values of the percentage of Pb extraction. The results of the correlation coefficient revealed positive relation between each two variables and confirmed the mutual interaction between the three studied parameters (temperature, time and acid concentration) on the extraction efficiency of Pb
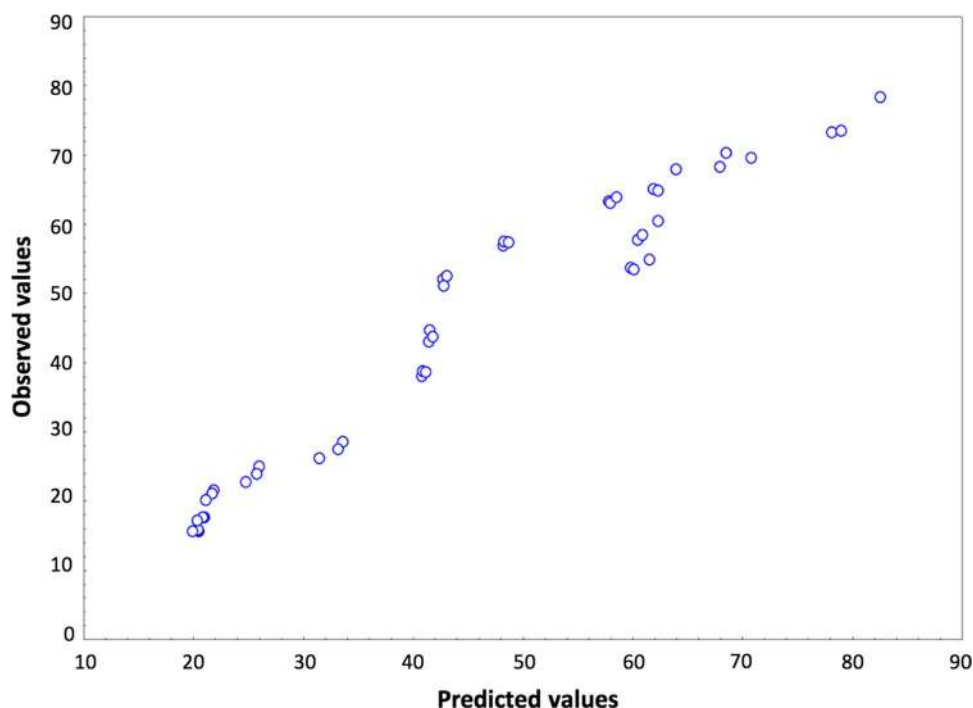
The effect of concentration

In the first 30 min, the leaching showed a burst mode for all three concentrations of HNO_3 at each temperature, after which it progressed at a lower rate. After 2 h, the leaching efficiency increased very slowly and almost reached plateau at 12 h. At 25 °C (Fig. 2a), extraction slightly decreased with increase in acid concentration. At 70 °C (Fig. 2b), similar extraction trends were observed, whereas at 95 °C and 3 M HNO_3 (Fig. 2c) slightly higher extraction was observed. However, the differences in extraction due to concentration were insignificant at all temperatures, implying potential for an economically higher efficiency using 0.5 M HNO_3. The relation between metal extraction and solubility of extracted product is further discussed in the Supplementary Material.

The effect of temperature

Extraction results were averaged for each temperature as shown in Fig. 2d. Extraction in the first 30 min increased rapidly with increase in temperature, implying a positive effect. After 30 min, extraction was 15%, 40% and 55% for 25 °C, 70 °C and 95 °C, respectively. Although the leaching kinetics increase with temperature, the extraction percentage at 30 min compared to the final leached amounts remains the same for all three temperatures, accounting for 75%. Therefore, repeated cycles with 30 min processing time could be designed to maximise metal extraction. Overall, the highest Pb extraction (78%) was achieved by 3 M HNO_3 at 95 °C after 12 h of leaching. The results further indicate

that although metal ions are firmly fixed in the crystal glass structure rendering extraction under normal conditions highly unlikely (Singh et al. 2016), mechanical activation of the glass successfully destroyed the glass inner structure, thus facilitating easy dissolution of higher amounts of Pb (Yu et al. 2016).

The results are comparable to a similar study on Pb extraction, but in alkaline solution, where maximum extraction was 67% after 2 h of extraction in 5 M NaOH solution at 80 °C (Zhang et al. 2016). Although the concentration (0.5 M) in the current study is lower than 5 M in the previous study, the extraction range and time required are similar. Contrarily, higher Pb extraction efficiencies through reduction-melting have been reported (Jani & Hogland. 2017; Zhang et al. 2016), although these methods are very energy-intensive compared to the current study.

Statistical analysis

According to the statistical results shown in Fig. 3 and Table S2, the proposed polynomial equation fits the experimental results quite well with a high correlation coefficient ($R^2 = 0.9901$). In Fig. 3, the results of the correlation coefficient revealed positive relation between each two variables and confirmed the mutual interaction between the three studied parameters (temperature, time and acid concentration) on the extraction efficiency of Pb. When R^2 approaches ± 1, the relationship between the two operating conditions is linear with high interaction between the two variables. In a comparison of all the variables with recovery, a One-way

ANOVA analysis of the difference among the variables of the proposed model equation showed that the results were significant ($P < 0.05$).

Conclusion

Extraction of Pb from contaminated crystal glass waste was investigated to achieve decontamination and resource recovery. Glass samples were mechanically activated and leached with nitric acid (HNO_3), focusing on the effects of leaching temperature, time and acid concentration on extraction efficiency. Mechanical activation of the glass enhanced Pb extraction significantly during acid leaching, making it a vital complimentary step to traditional leaching techniques. The first 30 min of reaction were important for the extraction since about 75% of the final extracted amounts was already extracted within this time, with lower leaching rate observed beyond the 30 min. This indicates potential for shorter reaction time with optimised experimental parameters favouring 30 min. Acid concentration also showed insignificant effect on extraction efficiency, which indicates economic feasibility through the use of lower acid concentration for similar results. Temperature, on the other hand, showed the highest effect on extraction efficiency. Overall, the highest extraction achieved was 78% in 3 M HNO_3 and at 95 °C. This study introduces mechanochemical extraction of Pb from crystal glass as a lower-energy alternative to pyrometallurgy, which could contribute to glass decontamination and resource recovery.

Compliance with ethical standards

Conflict of interest The authors declared no conflicts of interest.

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