Batch Leaching to Enhance Dissolution of Siliceous Secondary Materials for Controlling AMD Formation

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Abstract

Silica may be important for AMD control as it provides long-term neutralization and chemically passivating pyrite through secondary mineralization. This study tested several side streams of siliceous materials, i.e., Si-Mn slags and waste rock, in a batch leaching at various pH conditions and leaching reagents to evaluate the most optimum conditions to obtain silica through enhanced silicate dissolution. Leaching samples in MQ water resulted in a low Si release, whereas leaching of materials in carbonated MQ resulted in a high Si release. Dissolution of water-granulated slag in carbonated MQ released a high concentration of sulfur and manganese.

Keywords: Acid mine drainage, pyrite, silica, waste rock, slag

Introduction

Acid mine drainage (AMD) is a substantial environmental concern at mining sites, primarily resulting from sulfide oxidation. When exposed to oxygen, reactive sulfidic minerals, mainly pyrite, oxidize and release sulfate, acidity, and metal(oid) ions associated with the sulfide. In cases where AMD has already formed, the acidic discharge is typically treated by actively adding alkaline substances, such as lime, limestone, NaOH, or other materials capable of neutralizing the pH. However, long-term reliance on such treatments is not ideal due to the high costs associated with the continuous consumption of additives. Prevention measures to control AMD are the best available technique and are usually less costly than remediation. Passivation, also known as inhibition, is a preventive approach for controlling AMD. The principle of inhibition is based on forming a coating layer on the pyrite surface, which prevents surface oxidation, dissolution or adsorption (Li *et al.* 2024), thereby controlling long-term pyrite oxidation and AMD formation. Silica, due to its abundance in nature and environmentally benign characteristics, is considered superior to phosphate and other organic coatings.

Previous studies have demonstrated the effectiveness of silicates in inhibiting pyrite oxidation by forming a stable silicate-based coating on the pyrite surface (Butar Butar *et al.* 2025, Fan *et al.* 2017, Kollias *et al.* 2018,). Silicate coatings have been shown to remain stable within the pH range of 2.5–4.0 (Evangelou 1996), precipitate at circumneutral pH (Bessho *et al.* 2011) and form protective layers through adsorbed silicates or SiO2 precipitates (Kollias *et al.* 2018). In a study by Butar Butar *et al.* (2025), a single addition of an alkaline silicate solution without a pH buffer or adjuster, along with prolonged contact time with pyritic waste rock, managed to suppress pyrite oxidation and metal leaching by forming a silica (SiO2) layer on the waste rock surface. To ensure field applicability, which often involves complex chemical reactions that alter pH, using readily available siliceous materials rather than chemical reagents to minimize continuous amendment consumption and associated costs is preferred.

Therefore, batch leaching of siliceous materials can be employed to provide preliminary insights into enhancing the silica dissolution from several materials by evaluating the effectiveness of various leaching reagents, such as Milli-Q (MQ) water, carbonated MQ and alkaline solutions. The materials to be tested as a potential source of silica are andesitic waste rock and slags. This study aims to assess the release of silica by leaching siliceous materials under different chemical conditions to determine whether the silica released during leaching can serve a function in inhibiting pyrite surfaces. The focus of this study is to provide a preliminary understanding of siliceous materials originating from secondary sources to screen their potential suitability to be used to control AMD formation. The use of secondary resources and waste streams as sources of silica, aligns with the European Union's waste management and sustainability directive (the EU's Waste Framework Directive/Directive 2008/98/EC), promoting a circular economy and reducing overall environmental impact by waste stream valorization.

Materials and methods

Materials

The materials utilized in the batch leaching experiment consist of waste rock (herein referred to as WR) from an active polymetallic Cu-Zn-Au-Ag open-pit and underground mining operations in the Kristineberg area in Northern Sweden. The selected waste rock samples contain an average sulfur content of 11%, which corresponds to the sulfur concentration in the waste rock heap. Following collection, the waste rock underwent crushing, splitting, and homogenization.

Water-quenched, or more commonly known as water-granulated Si-Mn slag (SW) is an oxide slag produced during the manufacture of Si-Mn alloys. This slag results from the rapid cooling of molten slag through water quenching, leading to its rapid solidification and forming fine, granulated particles with a glassy, amorphous structure (*the anonymous company supplying the slag, personal communication, 14 November 2023*). Air-cooled Si-Mn slag (SA) is another by-product formed during the production of Si-Mn alloys, which results from the slow cooling of molten slag containing a mixture of Si, Mn, and other trace elements, using air. Air-cooling with water spraying gives an 90% amorphous, glassy surface whereas water-granulation gives a fine-grained, 100% amorphous and porous slag. SA and SW (herein referred to as the slags) used in this experiment were supplied by an anonymous metal company. The waste rock is andesite and contain silicate rock-forming minerals, whereas the slags comprise mainly amorphous silicate glasses (i.e., 100% amorphous glass in SW and up to 90% amorphous glass phase in SA and very few crystalline phases). For simplicity, the term silicate minerals are used throughout this article.

Methods

Before the batch leaching experiments, all solid samples were prepared and pre-treated as necessary, including size reduction to increase the reactive surface area and enhance the leachability of the materials. The waste rock was crushed to a particle size of less than 100 µm, similar to the particle size of the DST sample. The SA and SW samples, with particle sizes ranging from <100 µm to 1 mm, were used as received from the metal company and were not further reduced, except for sieving prior to use, where the <100 µm was used for the leaching experiment. To analyze the chemical composition before the batch leaching test, the solid samples were digested with two methods, i.e., acidic digestion with $HCl/HNO_3/HF$ in hotplate according to SE-SOP-0039 (SS-EN 13656:2003) and fusion with $LiBO_2$ according to SE-SOP-0060 (ASTM D3682:2013, ASTM D4503:2008) A sample weight of 100 g (± 0.001 g) was used for each leaching trial.

The leaching tests were conducted using various leaching solutions, including MQ water (herein referred to as MQ), carbonated MQ, and alkaline residual materials, to achieve initial circumneutral, acidic, and alkaline pH conditions, respectively. The leaching tests were carried out in three stages, with different liquid-to-solid (L/S) ratios and leaching durations. In the first stage, the L/S ratio was set to 0.75 (i.e., 75 mL of liquid), and the solid samples were leached for 6 hours. In every leaching stage, fresh solution and materials were added into high-density polyethene (HDPE) bottles. In the second and third stages, the L/S ratios were adjusted to 1 and 1.5, with leaching durations of 18 hours and 72 hours per stage, respectively. During the leaching process, the solid samples were mixed with the leaching solutions in HDPE bottles and agitated at 10 rpm using an end-over-end agitator. In set-ups involving carbonated MQ, MQ water was carbonated by pumping CO_2 directly into the water using a SodaStream, utilizing the principle of CO_2 dissolution in water to produce aqueous CO_2 ($CO_{2(aq)}$) and form H_2CO_3 (carbonic acid). In set-ups involving carbonated MQ, the solution added at each step was newly carbonated. The bottles were closed immediately, and lids were sealed thoroughly to limit CO_2 exchange with the atmosphere. In samples with mixtures (WR+SW), 4 wt% of SW was added to WR and was mixed homogeneously and leached in MQ.

At the end of each leaching step, leachate samples were collected and analyzed for pH and electroconductivity (EC) immediately. The leachate was filtered using a 0.2 µm filter (Merck Millipore) and subsequently analyzed for metal concentrations using Inductively Coupled Plasma – Sector Field Mass Spectrometry (ICP-SFMS) at ALS Scandinavia in Luleå, Sweden. Reagent blanks were also sampled and analyzed. The metal concentrations from all experimental setups were corrected by subtraction with the blank values to remove contributions from the reagents.

Results and discussion

Material characterization

The waste rock sample is andesite and contains several rock-forming silicate minerals, e.g., albite ($NaAlSi_3O_8$), biotite ($K(Mg,Fe)_3(AlSi_3O_{10})(OH)_2$), diopside ($CaMgSi_2O_6$), plagioclase $(Na,Ca)(Al,Si)Si_2O_8$, microcline ($KAlSi_3O_8$), and muscovite ($KAl_2(AlSi_3O_{10})(OH)_2$), among others (Butar Butar *et al.* 2025). The primary aim is to enhance the weathering of these minerals to facilitate the release of Si for pyrite passivation. Both slag types (SA and SW) contain an amorphous glassy silicate phase, which serves as a potential Si source, as well as soluble $Ca(OH)_2$, which provides alkalinity. The slags contain minimal crystalline phases.

The concentrations of selected major elements in the starting materials are presented in Table 1. The chemical compositions of SA and SW are identical, as both samples originate from silicomanganese slag and are characterized by high Mn and Si content, although the morphology and physical properties differ. In andesite waste rock, Si is primarily hosted in silicate rock-forming minerals, whereas sulfur is only associated with pyrite (FeS_2).

Leaching characteristics of materials

Overall, leaching materials in MQ water generated leachate with varying pH levels. The dissolution of andesitic waste rock in MQ water yielded a circumneutral pH (~6) (Fig. 1). Since pH is a critical geochemical factor influencing silicate weathering rate (Dupla *et al.* 2025), this study also examined dissolution of materials under acidic and alkaline conditions to compare with leaching at circumneutral pH. The pH of solutions resulting from dissolution in carbonated MQ (Fig. 1) was influenced not only by the dissociation of carbonic acid in water but also by the dissolution of the reactive buffering minerals, such as Ca(OH)2 in slags and silicate-bearing rock forming minerals in WR, in the presence of carbonic acid.

A similar trend of high pH was observed in the leachate of the slag samples, likely due

Table 1 Elemental analysis of WR and slag samples.

Material	Al	Ca	Fe	K	Mg	Mn	Na	S	Si
SA	90400	169000	6440	7980	57100	63000	3880	4980	198000
SW	82600	178000	5570	6250	47500	50600	2970	4400	211000
WR	79200	4830	69200	20500	42300	1370	2340	50900	263000

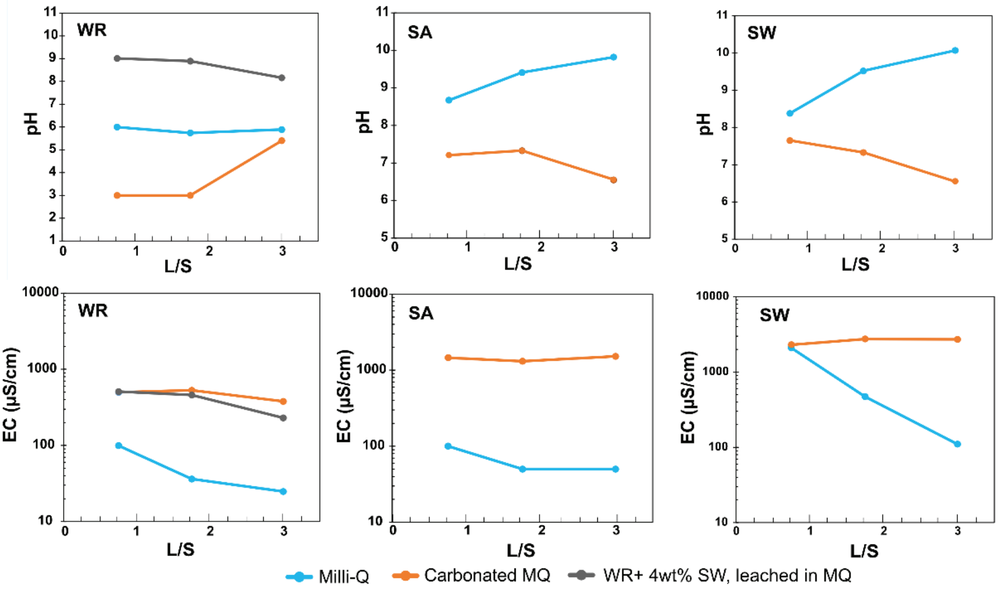


***Figure 1** pH and EC in the leachate samples, collected in the 3-step leaching test*

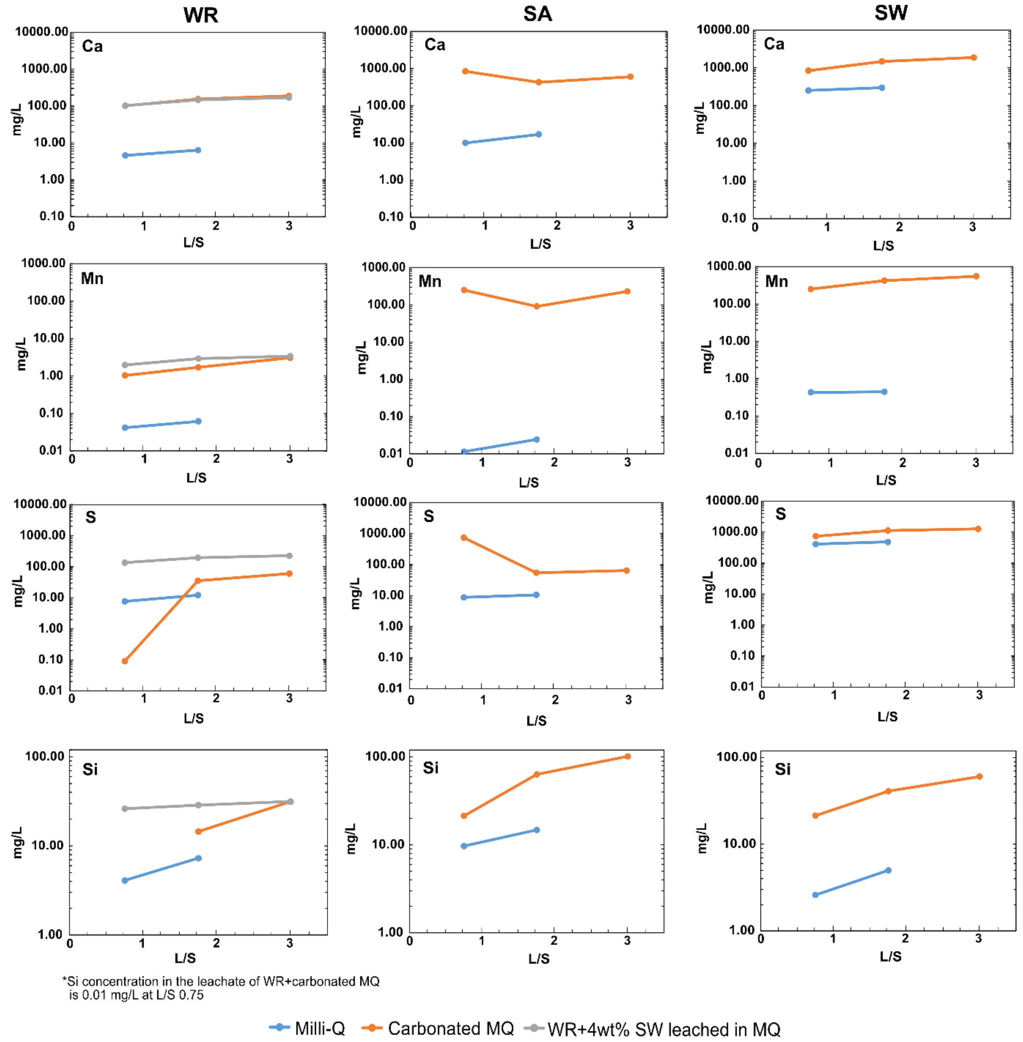
to dissolution of $Ca(OH)_2$. The elevated EC in the slag leachates corresponded to the increased concentration of the dissolved metals in solution (Fig. 2). The dissolution of SW in MQ resulted in leachate with a higher EC than that of SA (Fig. 1). The analysis of anions confirmed the higher EC and indicated that SW released more Cl ions compared to SA, attributed to the dissolution of salts in SW upon contact with water.

Overall, leaching the materials in MQ at circumneutral pH resulted in lower Si concentrations in solution compared to other pH conditions (Fig. 2). Fig. 2 demonstrates that silica dissolved from siliceous materials more effectively in carbonated water than in MQ water, as shown by the higher Si release observed under carbonated conditions. The batch leaching test further confirmed that carbonation of water promoted the dissolution of silicate minerals. Among the experimental setups, SA dissolution in carbonated solution yielded the highest accumulated silica concentration (~100 mg/L Si) (Fig. 2). The accumulated Si concentration in the solution followed the order: SA+ H_2CO_3 > SW+ H_2CO_3 > WR+ H_2CO_3 > WR+4wt%SW > SA in MQ > WR in MQ > SW in MQ.

In addition to Si, leaching the materials with carbonated water also resulted in a high Ca concentration in the solution (Fig. 2). Upon carbonation, Ca(OH)2 in the slags dissolved more rapidly than in MQ. Furthermore, the trilinear diagram (Fig. 3) indicates that Ca is the dominant cation in solution under acidic conditions following carbonation. The silica released during carbonation likely originated from Ca-bearing silicate minerals (Fig. 3). It is well-established that the dissolution rate of silicate minerals is pH-dependent and carbonic acid can promote silica dissolution by enhancing the dissolution of rock-forming silicate minerals through acid hydrolysis (Dupla *et al.* 2025). When silicate minerals react with carbonic acid, the accelerated weathering of silicate minerals sequesters CO2 directly in the form of alkalinity, primarily as bicarbonate ions, but also dissolves silica. The observed shift in the trend of major cations in WR (Fig. 3) likely suggests that the increased weathering rate of Mg-silicate minerals, such as biotite and diopside, occurred at low pH (Palandri and Karaka 2004) following carbonation, compared to MQ water.

Conversely, mixing waste rock (WR) samples with SW resulted in leachate with an initially alkaline pH due to the dissolution of Ca(OH)2 from the slag. However, as the available lime was depleted over time, the leachate pH gradually decreased (Fig. 1). The addition of the alkaline amendment

(SW) to WR also enhanced the dissolution of silicate minerals (Fig. 2). It is well-established that at pH>8, the Si-O bonds in silicates are weakened due to polarization from charged surface species, leading to the detachment of silicon atoms, and contributed by hydrolytic weakening by water dipoles (Brady and Walther 1989). Long-term albite dissolution, for instance, is proportional to silica surface charge above pH 8 (Brady and Walther 1989). Beyond the high Si concentrations observed in the solution, the selection of suitable materials should also consider the potential co-release of other elements upon carbonation or mixing with alkaline amendments. Although mixing materials with alkaline amendment (slags) improved silicate dissolution, it also facilitated the mobilization of deleterious elements. For instance, Mn was released in high concentrations when the materials were dissolved in carbonated water (~230 mg/L Mn in SA, ~553 mg/L Mn in SW), or when andesitic WR was mixed with SW, sulfur was released in high concentration in the leachate (~227 mg/L S) (Fig. 2). Finally, this study demonstrated that the dissolution of WR, SA, and SW in carbonated water effectively enhanced silica release.



*Si concentration in the leachate of WR+carbonated MQ is 0.01 mg/L at L/S 0.75

Figure 2 Cumulative elemental concentration released to the leachate, collected in the 3-step leaching test.

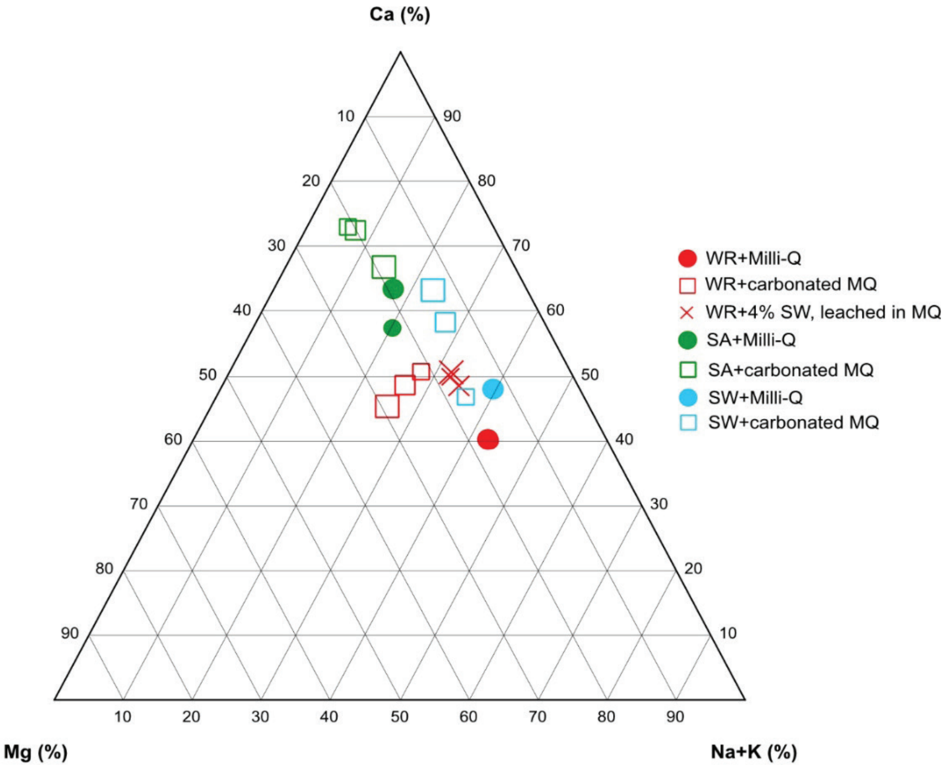


Figure 3 Trilinear diagram of the major cations in the leachate from all collected samples.

Conclusions

- The dissolution of siliceous materials in MQ resulted in circumneutral-alkaline leachate pH.
- The slags are inert to leaching in MQ and similarly, the dissolution of silicate minerals in andesite waste rock is slow in MQ.
- Carbonation of MQ used in the batch leaching test enhanced the dissolution of silicate minerals. Higher Si concentration was observed in samples dissolved in carbonated water than in MQ.
- Mixing WR with alkaline amendment (the slags) or using leachate from SW in the batch leaching test slightly improved silicate dissolution but is associated with a high release of Mn and S in the leachate.

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