

The effects of milling media and recycled water on pulp chemistry and flotation performance for single-mineral and mixed sulfide ores

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Abstract

In various mineral assemblages, targeted minerals often coexist with base metal sulfides, which may hold value for beneficiation and can significantly impact the metallurgy of the ore. Gaining insights into sulfide behaviour, both independently and within a mixed ore context, as examined in this study, assists in developing effective flotation strategies. Processing complexity increases with closed-water circuits that introduce residue from previous cycles. This study investigates iron (Fe) dissolution from minerals and milling media under varied water compositions related to gangue dissolution. It focuses on scenarios both with and without mineral Fe (pyrite vs. galena) and milling media Fe (forged steel vs. ceramic media). Furthermore, the study monitors mill pulp chemistry in situ under both controlled and natural pH conditions, examining electrochemical parameters such as mixed potential (Eh) and dissolved oxygen (DO), and correlating these with flotation performance. Complementary zeta potential and XPS data elucidate mineral surface phenomena under the investigated conditions.

Keywords: Sulfide minerals, milling media, ionic strength, pulp chemistry, closed water circuit, flotation performance

1 Introduction

Galena (Gn) and pyrite (Py) are common sulfide minerals frequently found together in ore deposits. Separating Gn from Py can be challenging, as it requires precise control of surface and pulp chemistry to effectively recover valuable minerals. This process becomes even more complicated with water recycling and can be heavily affected by the composition of the milling media used. For example, iron (Fe) ions are released from forged steel (FS) milling media, which complicates interactions within the cell by reacting with minerals and reagents. Figure 1 shows Fe-H₂O and Fe-H₂O-Xanthate Pourbaix diagrams, which are useful in determining the dominant Fe species under various redox potential (Eh)-pH conditions.

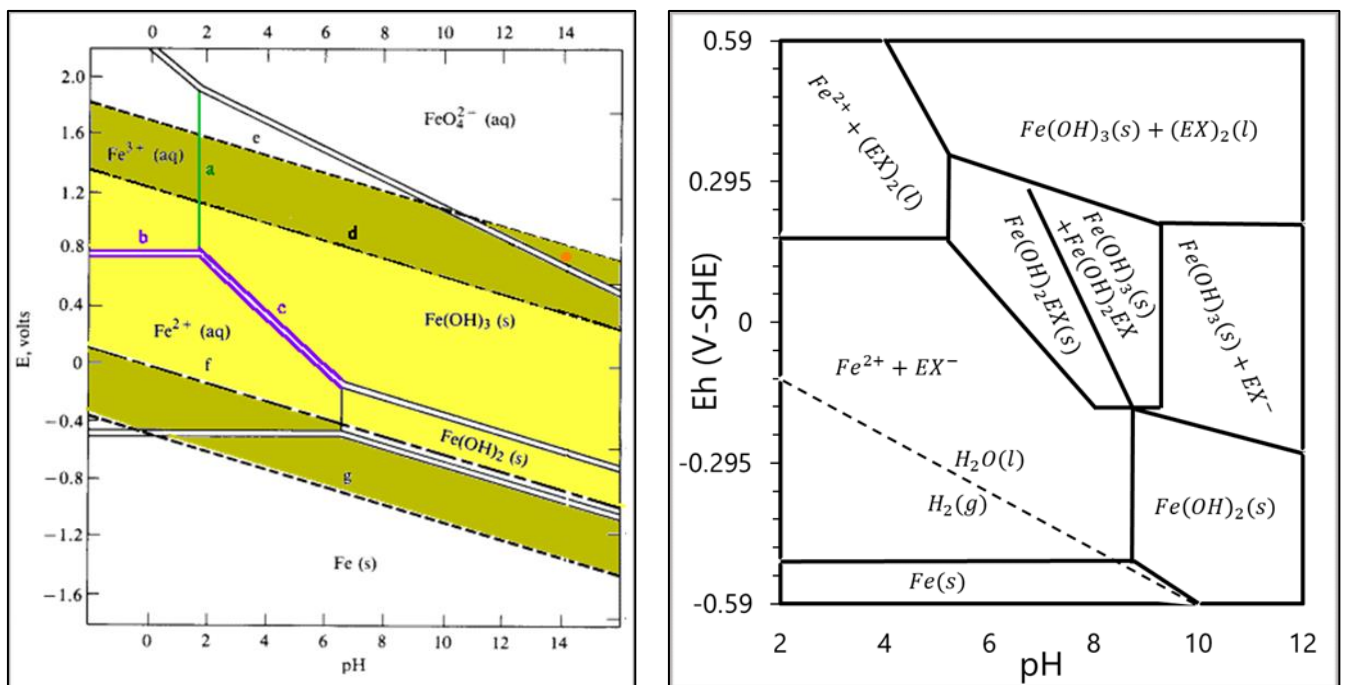


Figure 1 Eh-pH diagrams for Fe-H₂O [1] and Fe-H₂O-X [2] aqueous systems.

In sulfide milling, it is important to account for both inter-sulfide galvanic cells and those formed between the milling media and sulfide minerals (cf. Figure 2), since they can all significantly influence the electrochemical state of the pulp, leading to unexpected outcomes.

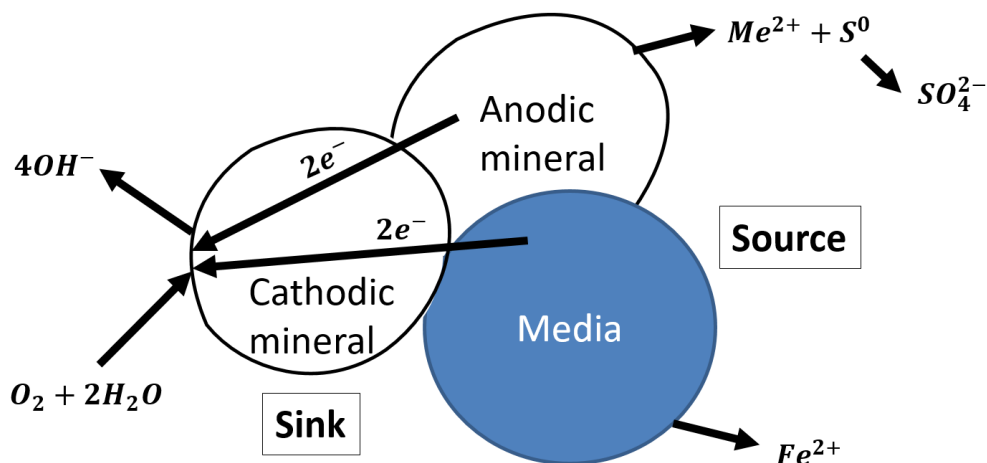


Figure 2 Galvanic interactions between a polysulfide mineral and Fe-bearing steel media.

2 Experimental

Pure samples of Gn and Py were obtained from Mineral World, South Africa, for use in the study. Mineral slabs were prepared for XPS studies and analysed independently in air, as well as after immersion in distilled water for 40 minutes, both with and without FS present. The slabs were dried using nitrogen gas and analysed with an ESCALAB 250 Xi XPS instrument (Thermo-Fisher Scientific, United States). In a separate test, 1 g powdered samples of either Gn, Py, or their 50/50 mixture were immersed in 300 ml of deionised water or synthetic plant water [3], [4] (1 SPW/0.0241 M) in a beaker within an ultrasonic bath. 1 ml aliquots were analysed for zeta potential using a Litesizer DLS 700 instrument (Anton-Paar, United States) after adjusting the pH to 4, 7, and 10. A parallel set of experiments was conducted adding $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ to the solution to achieve Fe concentrations of 40, 80, and 160 mg/l. Milling and flotation experiments were also conducted on the three ore variations, utilising a 2 kg mass of synthetic ore comprising 5% sulfide, 2% talc, and 93% quartz, with 2 L of either deionised water or 1, 3 or 5 SPW, and adding 100 g/t (40 mg/l) SIBX and 60 g/t DOW 200® frother. A Magotteaux® Mill (Magotteaux, Australia), designed to control and measure pH, Eh, and Do, and a 4.5 L Magotteaux® flotation cell were employed, and further analysis was conducted to measure concentrations of dissolved ions, SIBX, and Pb and Fe grades in the concentrates following procedures described in literature [5], [6]. All pH adjustments were performed with lime and HCl, except in the zeta potential tests,

where NaOH was used as the alkaline modifier. All experiments were duplicated, and the standard deviation for the duplicates is presented as error bars in the figures.

3 Results and Discussion

XPS results in Figure 3 show the impact of mineral exposure to air vs the aqueous conditions investigated. Oxidation product deposition on the mineral surface is observed to increase with the presence of FS, rising pH, and exposure to atmospheric air. Notably, in the absence of FS, there is less formation of oxidation products at pH 10 than 4 for Py, which corresponds with lower end-of-grind Eh (cf. Eh data in Figure 6) for the former. Thus, the oxidising potential of the pulp becomes an important factor to consider.

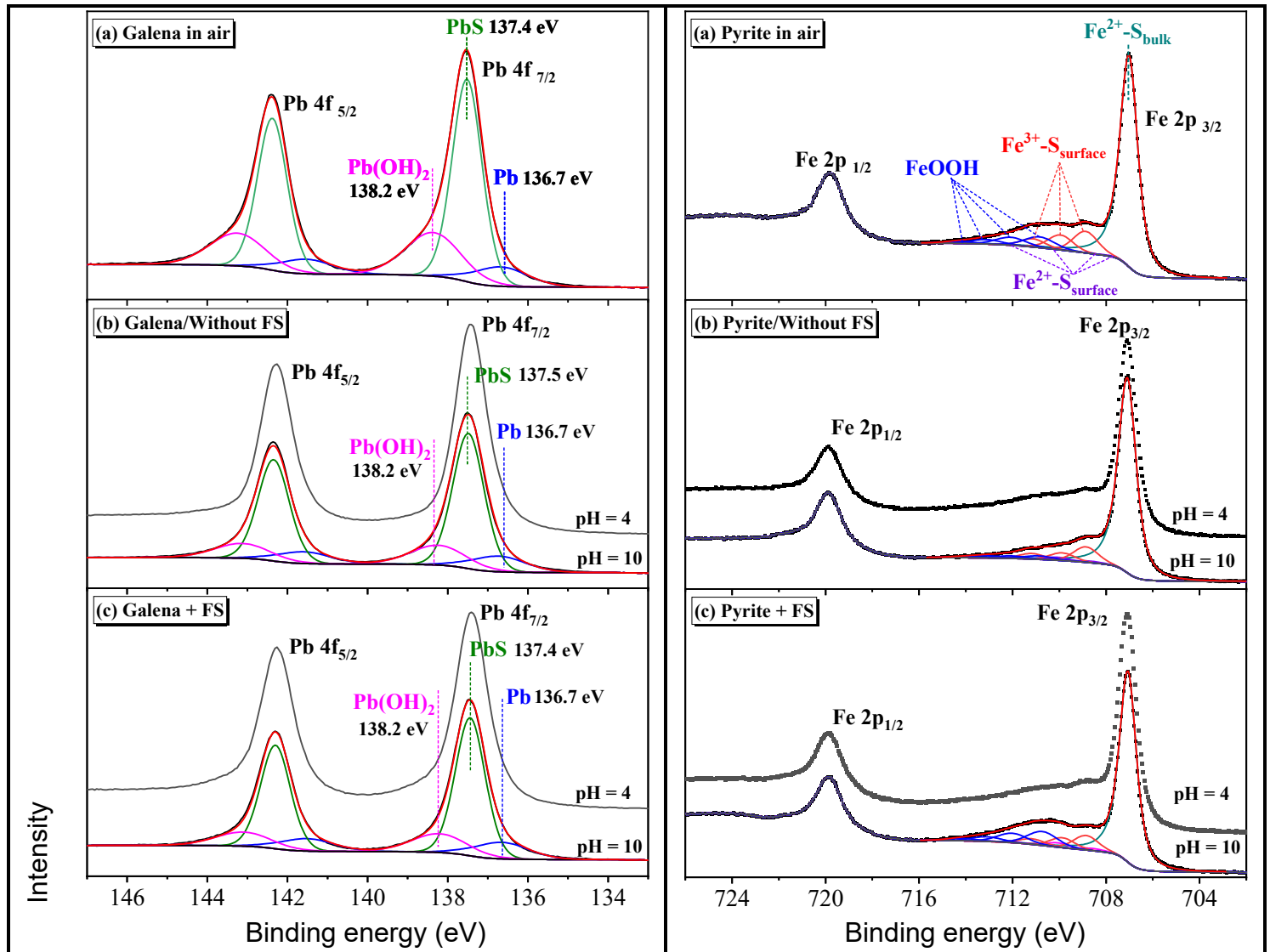


Figure 3 Impact of milling media composition on Py and Gn mineral surfaces.

The zeta potential data in Figure 4 indicate that a high pH generally promotes the formation of stable colloids, making flotation easier for both Py and Gn, with Gn exhibiting greater stability at high pH. Additionally, the presence of SIBX enhances colloidal stability at low pH, potentially improving floatability in these conditions. Data from mixed ore samples do not suggest a preference for the behaviour of any specific mineral. SPW appears to lower zeta potential, and the same is true for dissolved Fe ions, although the effect is minimal at the lowest concentration examined, 40 mg/l.

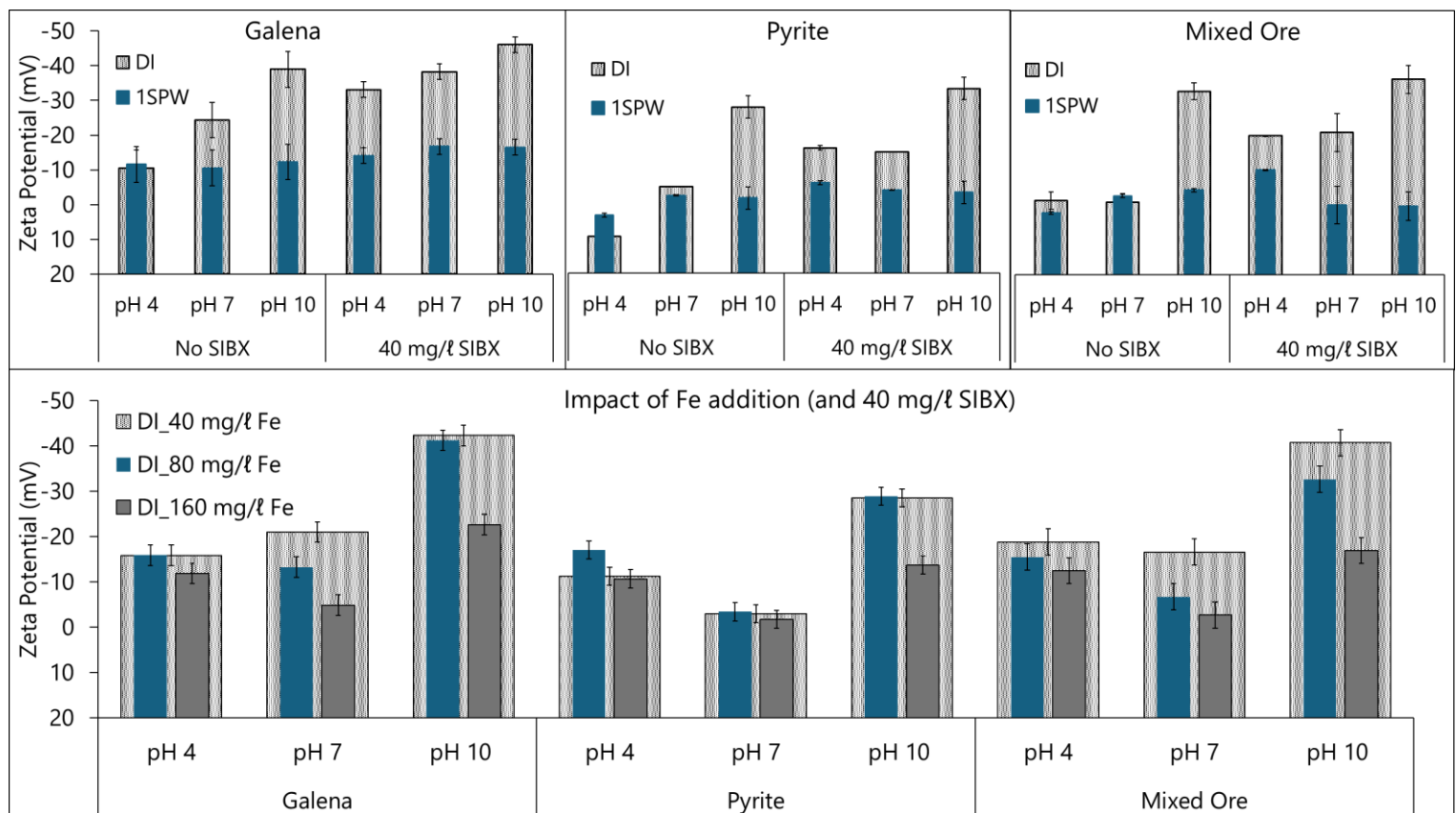


Figure 4 Effects of water composition, dissolved Fe on the zeta potentials of Py, Gn and the Mixed Ore under different pH conditions.

Figure 5 presents dissolution activity for different mineral variations. Dissolved Fe levels are similar for Gn and Py under all milling media conditions, indicating that in the FS case, the media is the main source of dissolved Fe [7]. The mixed ore case shows higher dissolved Fe, implying that more complex galvanic interactions in the pulp phase contribute to increased Fe dissolution. Significantly higher amounts of Pb dissolve into solution, which is logical since Gn has the lower rest potential in the

galvanic system [8], [9]. The effect of water type, shown by the comparison of DI and 5SPW, is most noticeable in Cer milling of the mixed ore, where SPW ions appear to enhance Pb dissolution.

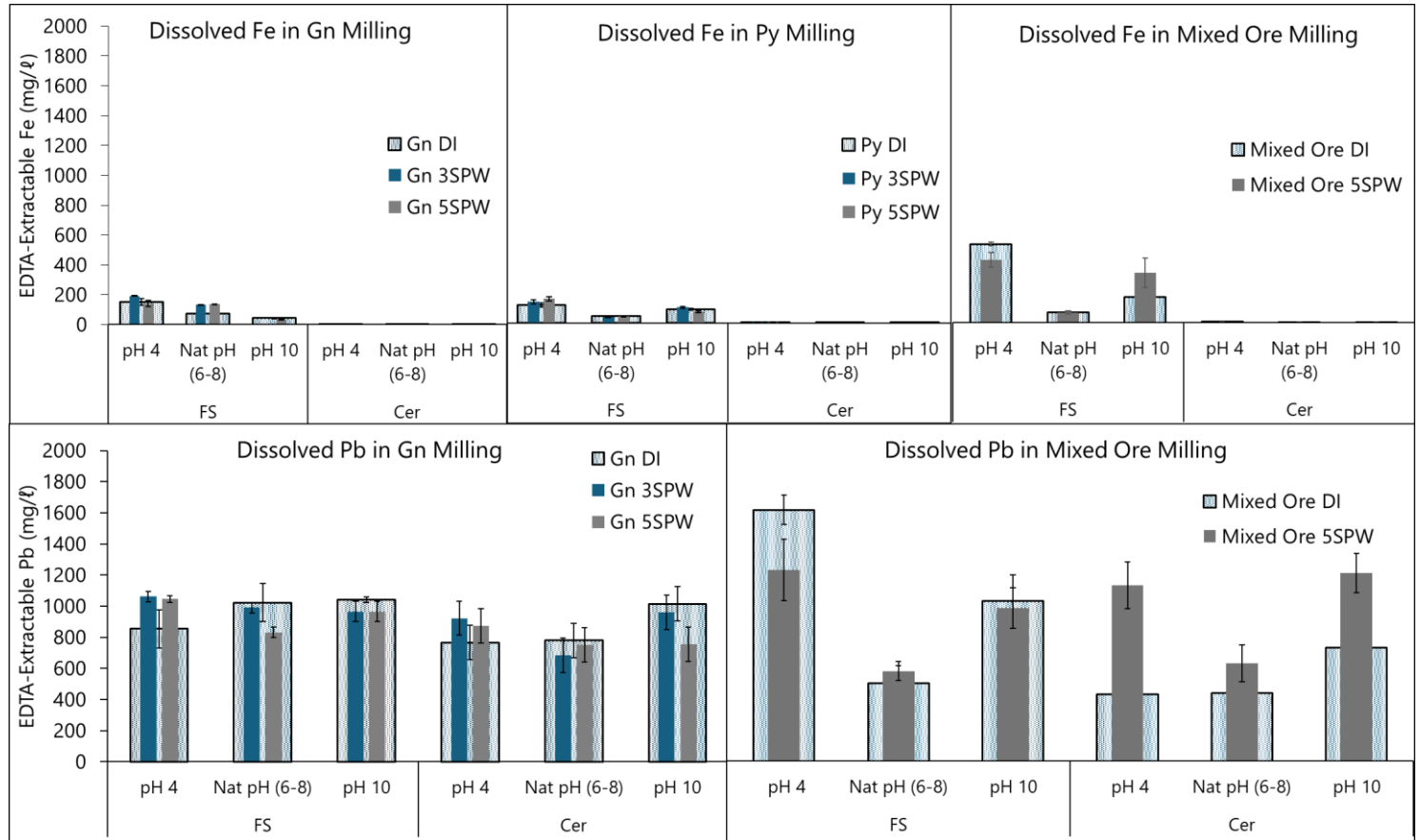


Figure 5 Impact of milling media and water types on Fe and/or Pb dissolution.

Residual SIBX and Eh data are commonly used to interpret flotation performance [10], [11], [12], [13]. Figure 6 explores whether there is a clear correlation between these two parameters. The data do not show a definitive relationship across different mineral types. However, within the same mineral type—particularly in the case of Py—higher Eh readings tend to correspond with lower residual SIBX concentrations, especially in feed slurry samples. The influence of water type on residual SIBX is most notable for Py under Cer milling conditions, aligning with the Eh data. Gn appears to cause significant SIBX consumption, likely reacting with the xanthate collector to form lead xanthate complexes [14], [15], which explains the low readings observed for Gn and the mixed ore. Overall, the Eh measurements support the idea that SPW ions create more reducing conditions.

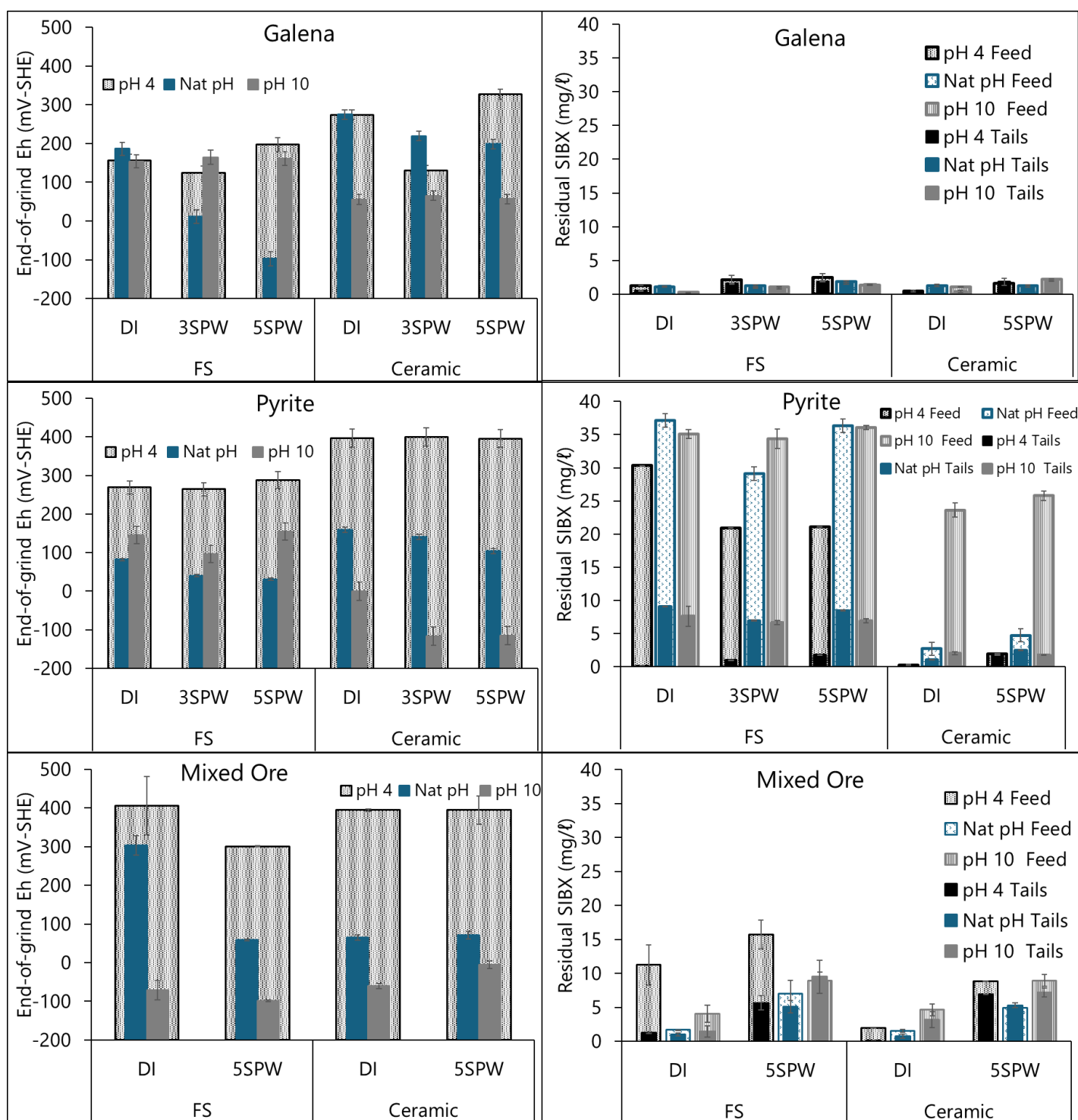


Figure 6 Impact of pulp phase reactions on Eh after milling and SIBX consumption during flotation.

The data in Figure 7 shows that a high pH leads to higher solids and water recovery for Gn, while the opposite is true for Py. The solids recovery for Gn at pH 10 is remarkably high, indicating froth overstabilisation. This aligns with the highest zeta potentials observed at pH 10 for Gn. The mixed ore case demonstrates consistent

recoveries across all pH, milling media, and water conditions, with a slight increase in water recovery at pH 10.

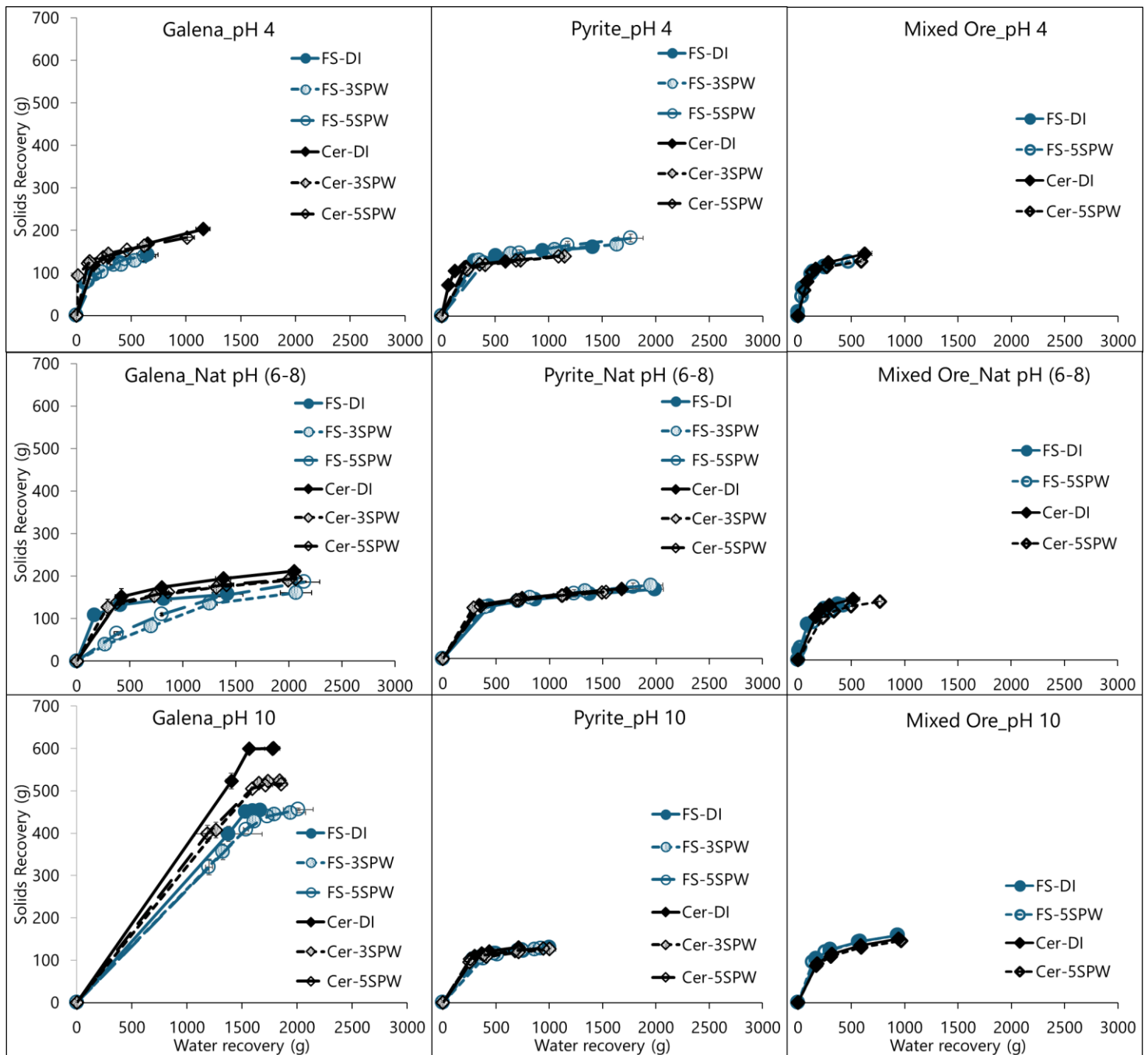


Figure 7 Solids and water recovery under the influence of various pH, water composition, and milling media conditions.

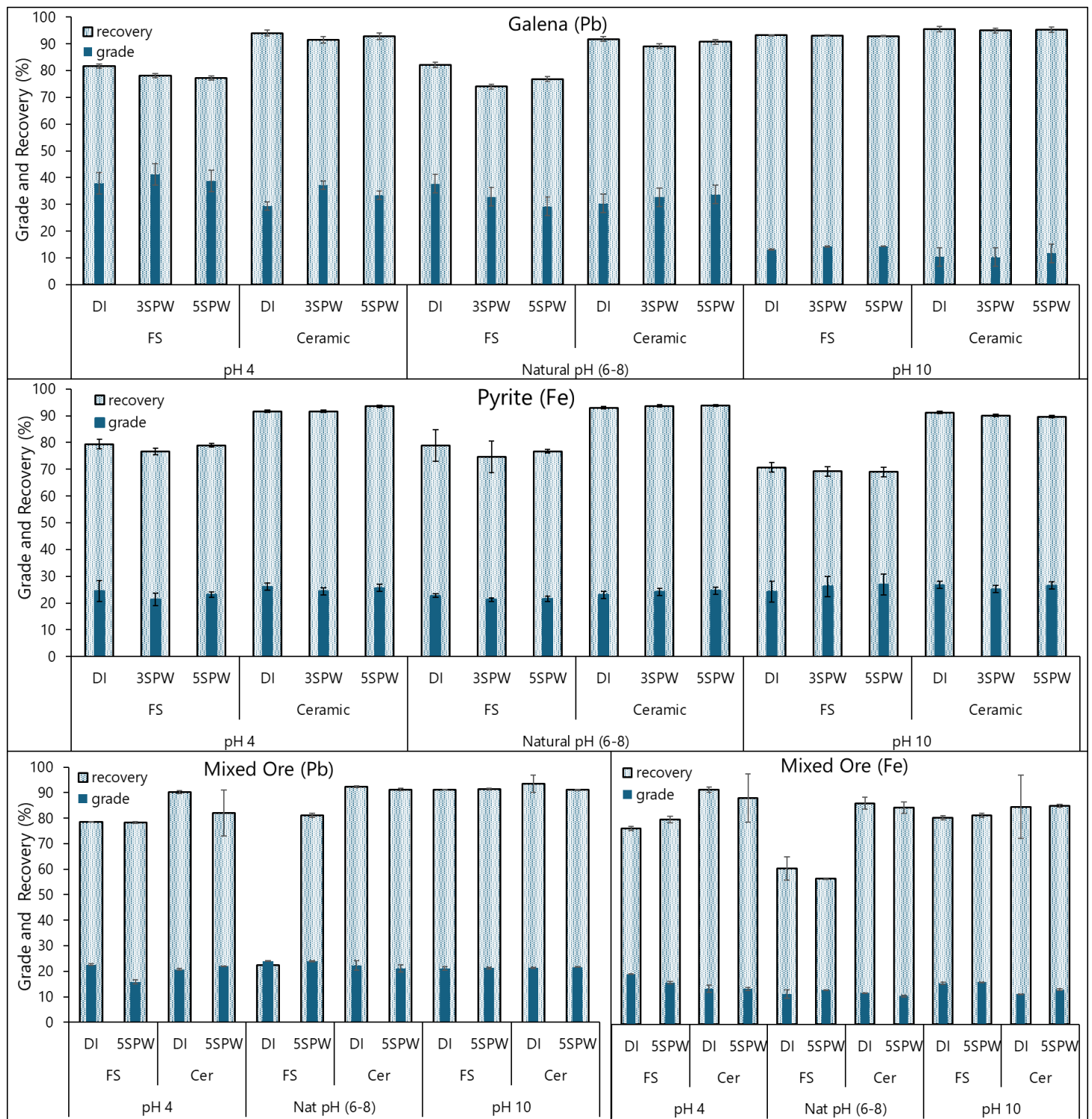


Figure 8 Grade-Recovery plots for Fe and Pb under the influence of various pH, water composition, and milling media conditions.

Figure 8 finally shows the grade-recovery data for the different conditions investigated. The highest Gn recoveries are observed at pH 10, and are comparable for all milling media and water conditions. Notably, the grades are lowest under this condition,

correlating to the froth overstabilisation effects shown in Figure 7. The same observation applies to Pb recovery in the mixed ore. Fe recovery in the Py case, on the other hand, is most reduced at pH 10, under FS milling conditions. This corresponds to the XPS data (cf. Figure 3), which shows that in the presence of Fe, the highest deposition of iron hydroxide and oxyhydroxide products occurs onto the Py surface, rendering the mineral less floatable.

4 Conclusions

The use of electrochemical and surface chemistry techniques to understand the impact of milling media and water composition on pulp chemistry and flotation performance has proved to be useful in this study. Overall, experiments with single minerals indicate that FS milling at high pH provides the most effective separation of Gn from Py. Nevertheless, a cleaning step would be necessary to enhance the grade of Gn in the rougher concentrate. These findings also apply to the mixed ore case, especially for Pb, where grade-recovery performance was comparable to that for Gn. However, the Py depression caused by dissolved Fe ions during FS milling of Py did not align with the higher recovery results seen in the mixed ore case, implying that the increased complexity of interactions when both sulfides are present can significantly influence process outcomes. On a positive note, the presence of SPW ions up to the highest tested ionic strength (5SPW/0.1205M) showed no substantial impact on process performance. This contradicts zeta potential predictions, which indicated reduced colloidal stability with added SPW ions, highlighting limitations in using this technique to predict ore floatability in water recycling scenarios. Additionally, residual SIBX and Eh data could not independently forecast the overall flotation behaviour across the process variations studied, emphasising the need for a combined approach of techniques to better understand chemical activity during milling and flotation.

5 References

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