

ORP modulation by NaCl in hydrochloric and sulfuric acid media: Influence of salinity and acid matrix

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Abstract: The beneficial effect of sodium chloride on the acidic leaching of sulfide minerals is widely reported and is mostly interpreted through surface-related mechanisms. However, its influence on the oxidation-reduction potential of acidic media, a key parameter governing solution stability and oxidation thermodynamics, remains insufficiently quantified. This work quantifies the effect of NaCl concentration on ORP in NaCl-HCl and NaCl-H₂SO₄ systems. ORP was monitored together with pH, conductivity, temperature and solution composition over acidity ranges up to 2 M and salinities up to 14 wt. % NaCl. NaCl alone produced only minor changes in ORP, whereas its addition to acidic solutions increased the measured potential with a strong dependency on the acid matrix. In NaCl-H₂SO₄ systems, ORP stabilized within a moderate potential range of approximately 580–640 mV (Ag/AgCl). NaCl-HCl systems exhibited two distinct regimes: a moderate regime comparable to that observed in sulfate media and a high redox potential close to 900 mV (Ag/AgCl) under high chloride concentration and strongly acidic conditions. Comparison with 1.6 wt. % FeCl₃ (approximately 0.1 M), used as a conventional oxidant benchmark, showed comparable ORP levels, highlighting the strong influence of NaCl on the measured redox environment under specific acidic conditions. Overall, the measured ORP reflected acid-matrix-dependent mixed-potential behaviour. NaCl modified the measured ORP under acidic conditions, whether present as background salinity or as an additive. However, solution acidity or chloride concentration alone could not produce the same redox potential response. The findings provide a quantitative basis for interpreting ORP behaviour in chloride-containing acidic systems and for evaluating electrochemical conditions relevant to hydrometallurgical process development.

Keywords: oxidation-reduction potential (ORP), sodium chloride, acidic saline systems, mixed-potential behaviour, pourbaix diagram, hydrometallurgy

1. Introduction

Hydrometallurgy as a metal-extraction technique relies on aqueous solutions to dissolve and recover metals. The efficiency and selectivity of metal dissolution are controlled by many physiochemical and electrochemical parameters like acid type and concentration, oxidation-reduction potential (ORP) of the solution, ionic strength and composition of the leachate (Winand, 1991; Bhargava et al., 2016). To modify these conditions and improve metal recovery, various additives are commonly introduced into leaching systems. For example, sodium chloride (NaCl), a common and inexpensive salt, has been reported to be used in acidic systems, resulting in higher leaching efficiency, particularly for sulfide minerals such as chalcopyrite (Carneiro and Leão, 2007; Jumbo-Pacheco et al., 2025). In the same context, seawater use is increasingly common in metal processing which has been reported to benefit chalcopyrite leaching due to its chloride content (Torres et al., 2015).

According to the literature, the positive effects of sodium chloride as a source of chloride ions are generally attributed to surface mechanisms and thermodynamic shifts in metal dissolution (Zhong and Li, 2019; Liang et al., 2012). The commonly cited explanations for NaCl-enhanced leaching are largely framed in terms of mineral surface reactions, with the main interpretations for chalcopyrite systems involving changes in surface properties, leaching kinetics and chloride complexation (Liang et al., 2012;

Mustafa et al., 2017; Carneiro and Leão, 2007; Kinnunen and Puhakka, 2004; Ping et al., 2009; Torres et al., 2015; Hernández et al., 2015). However, chloride ions sourced from this salt can also modify the electrochemical environment of the solution and cause the contribution of chloride to the bulk redox potential (Suslow, 2004; Winand, 1991; Senanayake, 2009; Seisko et al., 2020). ORP – together with pH – defines the thermodynamic stability of aqueous redox species and therefore influences whether metals remain in the dissolved form or not (Pourbaix 1966). Electrochemical studies on sulfide dissolution demonstrate that leaching performance is strongly potential-dependent: keeping the solution within an optimal ORP window promotes chalcopyrite dissolution and prevents passivation (Córdoba et al., 2008; Velásquez-Yévenes et al., 2010). Chloride containing systems show that the solution redox potential depends on its chemical composition and can correlate with dissolution behaviour, which means that chloride can influence the bulk electrochemical environment (Seisko et al., 2020). Furthermore, under electro-oxidation conditions, chloride can participate in oxidant-generating pathways, such as hypochlorite formation (Ping et al., 2009). These findings highlight the redox reactivity of chloride-containing media and support the need to evaluate ORP responses in chloride–acid matrices.

Selecting the leaching medium is a fundamental aspect of hydrometallurgical process design. While sulfate media remain as the industrial standard due to lower capital costs and established solvent extraction circuits, chloride-based systems often provide superior metal solubility and faster dissolution kinetics (Watling, 2013; Watling, 2014). Some studies have reported differing positive leaching responses in chloride- and sulfate-based systems containing NaCl and ferric oxidants (Carneiro and Leão, 2007; Sepúlveda et al., 2024). However, these investigations have primarily focused on mineral dissolution behaviour and surface-related mechanisms rather than on the electrochemical characteristics of the solution. Furthermore, the systems investigated by Carneiro and Leão (2007) involved HCl–NaCl–FeCl₃ and H₂SO₄–NaCl–Fe₂(SO₄)₃, where the chloride source, oxidant chemistry and acid matrix varied simultaneously, which makes it difficult to separate the contribution of NaCl in dissolution rate of the systems. This distinction is important because even under comparable acidity and salinity conditions, chloride containing systems may exhibit different redox behaviour in hydrochloric and sulfuric acid media.

Despite the use of NaCl in hydrometallurgical systems, a distinct gap remains in understanding how chloride addition influences the bulk electrochemical environment of acidic solutions particularly oxidation–reduction potential and the role of the acid matrix. Previous electrochemical studies of chloride-assisted leaching have mainly focused on the processes occurring at the mineral–solution interface, particularly mineral oxidation and dissolution kinetics, surface passivation and the influence of chloride in systems containing oxidants (Senanayake, 2009; Zhong and Li, 2019; Velásquez-Yévenes et al., 2010). In these studies, oxidation–reduction potential has generally been used as a process-control variable, in relation to mineral dissolution and leaching performance. However, isolating the effects of chloride from NaCl concentration and the acid matrix on the stabilized ORP of the bulk solution, independently of mineral dissolution, has received comparatively limited attention.

We hypothesize that the ORP of acidic NaCl-containing solutions depends on the interaction between NaCl concentration and the acid matrix rather than on chloride concentration or proton activity alone. We expect that NaCl addition would modify the stabilized ORP of acidic solutions with the trend of the response depending on whether HCl or H₂SO₄ is used. Under comparable acidity conditions, NaCl addition was expected to produce an overall positive change in ORP, while the ORP–NaCl concentration relationship was expected to differ between the two acid media. To test this hypothesis, stabilized ORP was measured in mV versus Ag/AgCl over defined ranges of NaCl and acid concentration in NaCl–HCl and NaCl–H₂SO₄ solutions. pH, conductivity and temperature were also monitored to support the interpretation of the ORP response. FeCl₃-containing solutions were also examined as a conventional oxidant benchmark. Together with selected physicochemical observations and thermodynamic interpretation, the ORP measurements were used to clarify the influence of NaCl on the redox environment of acidic solutions. This work provides a basis for understanding and evaluating redox conditions in chloride-containing leaching systems.

2. Materials and methods

2.1. Reagents and solution preparation

All experiments were conducted using distilled water as the base medium. Hydrochloric acid (HCl) and sulfuric acid (H₂SO₄), along with the solid materials; sodium chloride (NaCl, supplied as a commercial

salt with Na content: 39 g per 100 g) and anhydrous ferric chloride (FeCl_3 with 97% purity and density: $2.80 \text{ g}\cdot\text{cm}^{-3}$), were used to prepare synthetic acidic saline solutions. All media investigated in this research were prepared or diluted to the required concentrations before use. Each solution used for concentration calculations, was characterized in terms of mass fraction and density, as summarized in Table 1. In this study, all solution compositions were prepared and controlled on a mass-fraction basis to maintain consistency across experimental repetitions and to minimize uncertainties associated with volume-based concentration. This basis was selected because concentrations expressed in g/L or mol/L depend on the final solution volume and density, particularly in concentrated multicomponent electrolytes, where density and solution non-ideality vary with composition and volume cannot simply be assumed to be additive (Thomsen, 2009). The density and final volume of each solution were considered when calculating the corresponding g/L and molarity values. These units are reported only as secondary equivalents for comparison with commonly used concentration scales.

Table 1. Characteristics of prepared stock solutions

Solution	Sodium chloride	Ferric chloride	Sulfuric acid	Hydrochloric acid
Mass fraction (%)	25	26	98	35
Density (g/mL)	1.18	1.20	1.84	1.18

2.2. Experimental design

Different sets of experiments were designed to evaluate the influence of NaCl concentration on the oxidation–reduction potential of acidic saline systems. Two acidic media, HCl and H_2SO_4 , were investigated separately to compare chloride and sulfate-based environments under different concentration regimes. Experimental approaches including first baseline ORP profiling where individual reagents (H_2SO_4 , HCl and NaCl) were incrementally added to 200 mL of distilled water to assess the independent contribution of salinity and acidity to the redox environment. Subsequently, NaCl–acid systems were investigated under two main conditions:

- (i) Fixed-acid background: NaCl was gradually added to pre-prepared acidic solutions (0.5 M and 2 M H_2SO_4 or HCl), resulting in a gradual decrease in acid concentration.
- (ii) Acid-compensated addition: NaCl and acid were co-added, with back-calculated corrections to maintain a background medium with constant acid or salinity mass fraction and to minimize dilution effects.

The primary comparative conditions for the combined acid–salt systems were independently evaluated in duplicate using identical nominal solution compositions, preparation protocols and measurement procedures to assess the repeatability of the observed ORP response. Corresponding data are presented as mean $\pm$ standard deviation (SD). Complementary measurements were performed across varying conditions to characterize system behaviors, including: (i) FeCl_3 reference measurements under comparable conditions to examine ORP behavior in the presence of a conventional oxidant, and (ii) time-dependent ORP tracking to monitor potential stabilization kinetics. For these complementary evaluations, single-run results ($n = 1$) are reported, as the corresponding runs were not considered sufficiently equivalent to be combined as replicates.

2.3. Parameters measurements

With the focus on continuous measurements of ORP, other parameters like pH for physicochemical interpretation and estimation of hydrogen ion concentration, along with the conductivity and temperature for the influence of ionic strength and thermal variation were monitored throughout the experiments. For this purpose, Hanna Instruments HI5522 is used with the HI3230 ORP probe, the HI76312 conductivity probe with a cell constant of 1/cm and the HI7662-W temperature sensor. During the experiments, pH was measured using a separate intrinsic probe (HI11310) due to the limited accuracy of a dual-function electrode for simultaneous measurements of pH and ORP.

For precise redox potential measurements, the HI3230 ORP probe (Hanna Instruments) was used, featuring a platinum sensing pin, a polyetherimide (PEI) body, a single ceramic junction, and a gel-filled

electrolyte with an Ag/AgCl reference system. The exact KCl concentration of the internal gel electrolyte was not specified in the available manufacturer documentation. For the approximate conversion to the SHE scales, the reference potential was assumed to correspond to a concentrated KCl electrolyte in the range of approximately 3 M to saturation, consistent with the concentrated KCl electrolytes used in other single-junction Ag/AgCl electrodes from the same manufacturer. According to Hanna Instruments, conventional calibration is not required for its ORP electrodes. Therefore, the electrode was not calibrated; instead, its response was verified before each experiment using HI7022L ORP test solution, with an assigned potential of 470 mV at 25 °C. The electrode was rinsed with distilled water and immersed in the test solution until a stable reading was obtained. Probe performance was considered acceptable if the measured value was within ± 10 mV of the assigned potential, according to the manufacturer's specification. The electrode was then rinsed again with distilled water before the experimental measurements. When not in use between experimental sets, the electrode was stored at room temperature in Hanna Instruments HI70300 electrode storage solution.

2.4. Stabilization and homogenization protocol

All experiments were conducted under continuous magnetic stirring to maintain homogeneous solution conditions during reagent addition and measurement. Solutions were mixed continuously using same setting and configuration throughout the experiments. A stirring rate of approximately 250 rpm, estimated from the instrument setting, was maintained throughout all experiments. To ensure consistency among experiments, a standardized stabilization methodology was applied throughout the study. After each reagent addition, the solution was continuously stirred for approximately 5 min, and subsequently, an additional stabilization period of 3–5 min was allowed prior to recording the final values. Accordingly, all final values were recorded only after signal stabilization was observed, which helped us minimize fluctuations caused by the immediate effects of reagent addition.

Following the report by Suslow (2004) and our observations during the experiments, ORP values were interpreted as an operational window rather than a fixed point. Considering the fluctuation observed in the sensor readout (approximately 10 mV), a uniform measurement protocol was followed. Continuous parameter measurements were performed with a sampling interval of approximately 0.5 min during a sufficient mixing period of 5 to 10 minutes to distinguish transient ORP peaks from stabilized ORP values.

2.5. Data treatment, statistical analysis and thermodynamic assessment

For conditions tested in duplicate, the stabilized ORP values obtained from the two independent experiments were used to calculate the mean and standard deviation. The results are reported as mean $\pm$ SD, with error bars representing ± 1 SD in the corresponding figures. These duplicate measurements were primarily intended to assess the repeatability and variability of the observed trends. With only two independent replicates available per condition ($n = 2$), the basis for formal statistical inference was limited. For this reason, the inferential comparison between the HCl and H₂SO₄ systems was restricted to the independently duplicated fixed-acidity series. Although solution compositions are reported primarily on a mass-fraction basis throughout this study, the corresponding series were compared at the same nominal analytical acid concentration (approximately 0.5 or 2.0 M) and at the closest experimentally measured NaCl mass fractions. These nominal molarities were used only for defining comparable experimental series. Successive NaCl additions within a given experimental run were treated as serial observations and were not considered independent replicates. The HCl–H₂SO₄ difference was defined as $\Delta\text{ORP} = \text{ORP}(\text{HCl}) - \text{ORP}(\text{H}_2\text{SO}_4)$. A common repeatability standard deviation was estimated from the four independently duplicated fixed-acidity series and used to calculate two-sided 95% confidence intervals for the composition-matched contrasts. Because several contrasts were evaluated, p-values were adjusted using the Holm procedure (Holm, 1979). Welch tests based on the condition-specific replicate standard deviations were additionally performed as a sensitivity analysis. Considering the limited number of independent runs, all the inferential results were interpreted cautiously.

For the quantitative assessment of non-ideal solution behaviour, activity-corrected equilibrium boundaries were calculated for the fixed 7.1 wt.% HCl–NaCl series using the Pitzer electrolyte model at

25 °C. The use of this approach for concentrated NaCl–HCl solutions is supported by Nour et al. (2024), who applied Pitzer-type modelling at 298.15 K over ionic strengths up to 7.5 mol kg⁻¹. Pitzer-model-derived chloride and proton activities, together with water activity, were used in the Nernst expressions for the Cl₂(g)/Cl⁻ and O₂/H₂O equilibrium boundaries. Standard potentials of 1.358 V for Cl₂(g)/Cl⁻ and 1.229 V for O₂/H₂O versus SHE were used at 25 °C, assuming unit fugacity for Cl₂(g) and O₂(g), corresponding to the standard gas state of 1 bar under the ideal-gas approximation (Bard et al., 1985). For comparison, and to directly assess the effect of the activity correction, molality-based boundaries were also calculated by approximating activity with molality. The experimental ORP values were converted to the SHE scale using the Ag/AgCl reference-potential range of +0.197 to +0.210 V at 25 °C. The activity correction was applied only to the calculated equilibrium boundaries and not to the measured Pt-electrode potential, because the latter represents a mixed potential and the activities of the individual potential-determining redox species were not independently measured.

3. Results and discussion

In this section, the baseline ORP behaviour of the individual solution components and the interaction of NaCl in H₂SO₄ and HCl systems are discussed to evaluate the potential of this salt in modulating the oxidative environment of acidic solutions.

3.1. Baseline ORP behaviour of individual solution components

Data are presented in Fig. 1, showing the baseline ORP response during the independent addition of NaCl, HCl, and H₂SO₄ to distilled water. At concentrations below approximately 0.7 mol/L, both the HCl and H₂SO₄ systems increased the ORP from approximately 200 mV to 450–470 mV, while NaCl alone caused little change. At higher concentrations, the responses of the two acids became clearly different. The H₂SO₄ system remained relatively stable over most of the concentration range, whereas the ORP of the HCl system decreased, reaching about 315 mV near 2.0 mol/L. Although the smaller variations at high concentrations should be considered relative to the experimental error, the H₂SO₄ system was approximately 120 mV higher than the HCl system. The decrease in concentrated HCl may be associated with non-ideal ionic behaviour and changes in species activities at high ionic strength (Schneider et al., 2004). Chloride adsorption may also influence the response of the Pt electrode, which can lower the measured Eh (Priyantha and Malavipathirana, 1996). NaCl alone, as a source of Cl⁻ ions, produced only minor changes in ORP. Despite increasing salinity, the measured potential remained within a narrow range of approximately 180–200 mV.

The conductivity evolution of the same systems is presented in Fig. 2 as supportive physicochemical information. The results demonstrate that despite conductivity and oxidation reduction potential being influenced by increasing electrolyte concentration, both do not evolve proportionally. This behaviour

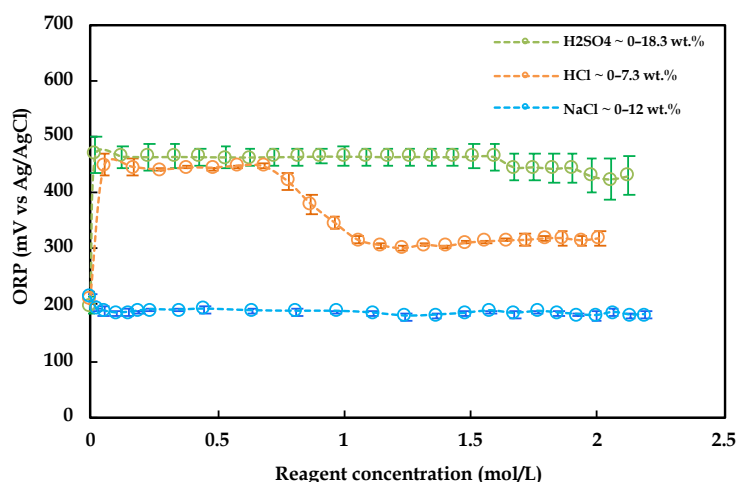


Fig. 1. Baseline ORP behaviour during independent addition of NaCl, HCl and H₂SO₄ in distilled water. Error bars represent the standard deviation of two independent experiments. The concentration ranges shown in the legend represent the experimentally prepared mass fractions of each reagent

suggests that conductivity primarily reflects charge transport properties, whereas ORP is governed by the prevailing redox couples and mixed-potential equilibria at the electrode surface (Schüring et al., 2000). As shown in the plot, NaCl caused a substantial increase in conductivity due to the higher concentration of dissolved ions. In contrast, both HCl and H₂SO₄ showed significantly higher conductivity than NaCl due to the high mobility of proton species in solution. Although HCl and H₂SO₄ differ in their dissociation behaviour and ionic speciation, both acids showed broadly similar conductivity trends within the studied concentration range.

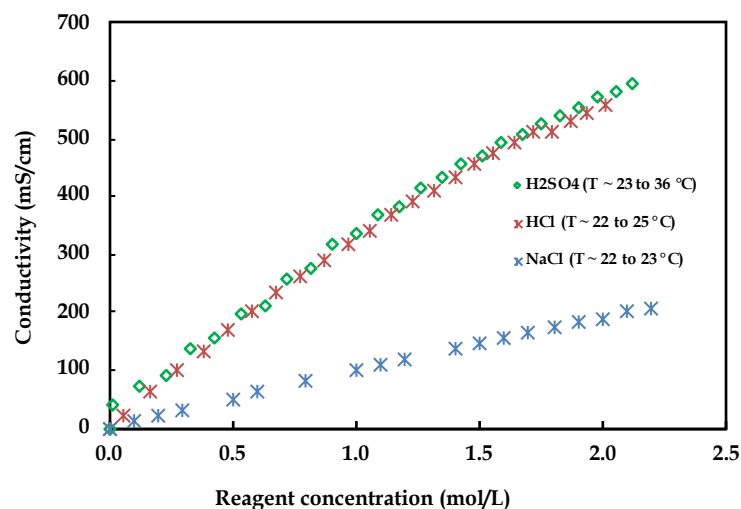


Fig. 2. Baseline conductivity evolution of NaCl, HCl, and H₂SO₄ systems in distilled water during incremental reagent addition, demonstrating the different ionic transport behaviour

3.2. ORP modulation in NaCl-HCl systems

Following the baseline characterization, the effects of salinity and acidity on ORP were investigated in NaCl-HCl systems. The focus was to understand the role of chloride concentration in modifying the redox environment of HCl acid solutions.

3.2.1. NaCl addition to HCl background with concurrent dilution

The first oxidative potential dataset, plotted in Fig. 3, is based on the incremental NaCl addition to solutions with concentrations of 1.8 and 7.1 wt.% HCl (approximately 0.5 and 2.0 M, respectively). As NaCl was added, the HCl concentration progressively decreased because of dilution. At zero NaCl, the initial ORP values for each solution were consistent with the baseline HCl behaviour shown in Fig. 1, where the lower HCl concentration shows the higher redox potential. As the NaCl concentration increased, the initially 1.8 wt.% HCl system approached a plateau near 637 mV, whereas the initially 7.1 wt.% HCl system approached approximately 597 mV. However, the more concentrated HCl system showed a larger overall increase in ORP, approximately +286 mV, compared with +136 mV for the 1.8 wt.% system. Comparing NaCl addition to distilled water, which exhibited ORP values of only approximately 200 mV, its addition to both acidic backgrounds caused a substantial increase in ORP. This comparison indicates that the measured response resulted from the combined acidic and chloride-containing environment rather than from NaCl or acidity alone, and the increase in ORP despite the progressive reduction in HCl concentration also shows that the response was not controlled solely by proton concentration. At higher NaCl concentrations, the incremental increase in ORP gradually approached a plateau. The conductivity measurements, recorded in the range of approximately 100–300 mS/cm, confirm that these measurements were obtained in concentrated ionic media, however the individual contribution of ionic strength was not quantified.

The positive ORP response observed in NaCl-HCl systems suggests that the measured potential is influenced not only by proton concentration but also by the presence of chloride ions and the overall ionic environment of the solution. However non-fixed background concentration affected by dilution,

limit a controlled view of the dynamic concentration profile during the test, so we cannot draw robust conclusions about component-specific effects. Therefore, to better isolate the impact of component concentrations, a second data set was extracted from different experiments where the compensated fraction of acid was added to maintain an approximately constant HCl mass fraction and minimize dilution effects.

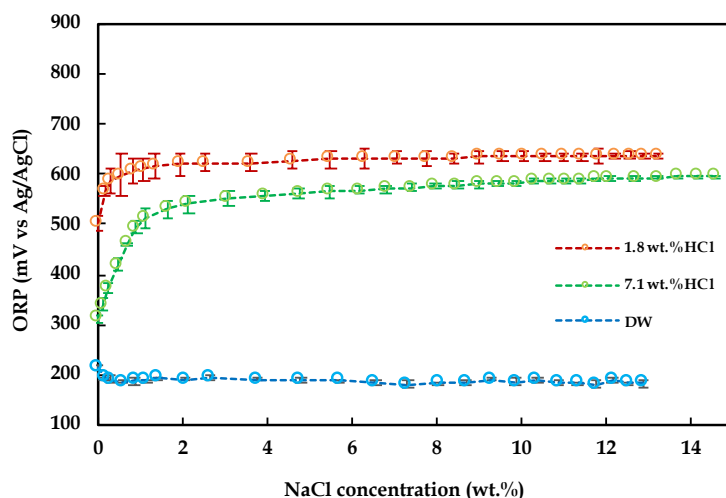
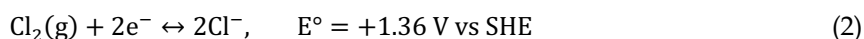


Fig. 3. ORP evolution during incremental NaCl addition into hydrochloric acid solutions under fixed initial acidity of 1.8 and 7.1 wt. % HCl, effected by progressive dilution. Error bars represent the standard deviation of two independent experiments

3.2.2. NaCl-HCl systems under fixed acidity conditions

Fig. 4 shows a non-linear ORP response to NaCl addition at fixed HCl concentrations of 1.8 and 7.1 wt. % (approximately 0.5 and 2 M, respectively). Based on this plot, up to approximately 10 wt. % NaCl, both systems showed similar ORP values, mainly within the range of 550–600 mV. At higher NaCl concentrations, when HCl was added to maintain the wt. % at around 7, it makes the solution strongly acidic ($\text{pH} < 0$), and the subsequent addition of more than 10 wt. % NaCl caused the redox potential to increase sharply to nearly 900 mV. This high-potential regime, observed at high NaCl concentrations under strongly acidic HCl conditions, is consistent with a chloride-dependent contribution to the mixed potential. However, because chlorine species were not measured during our experiments, this high-potential regime cannot be conclusively attributed to chlorine-related redox processes. Nevertheless, chloride-related interfacial reactions at the Pt electrode are electrochemically plausible in concentrated chloride media (Patil et al., 2011). If active chlorine was present, the low pH could shift its aqueous speciation toward dissolved molecular chlorine according to Eq. (1) (Cherney et al., 2006). The observed ORP values, after conversion to the SHE scale, remained below the standard potential of the Cl_2/Cl^- half-reaction ($E^\circ = +1.36 \text{ V vs SHE}$; Eq. 2), which is consistent with the Pt electrode recording a mixed potential rather than the equilibrium potential of a single redox couple (Bard et al., 1985; Stefánsson et al., 2005). Under the concentrated conditions used here, the equilibrium potential of this couple would depend on the activities of chloride and chlorine, as described by the Nernst relationship in Eq. (3). The strong non-ideal behaviour expected at high ionic strength also limits calculations based solely on analytical concentrations (Zimmermann et al., 2018). In the standard potentials section of the Aqueous Solutions book, a comparable oxidizing power scale is reported for HOCl/ClO^- systems under alkaline conditions (Eq. 4), although the dominant chlorine species are different from those expected in the present acidic chloride media (Bard et al., 1985). Further test results in higher concentrations, to 20% NaCl, show a similar plateau around 900 mV (Fig. 5). This ORP range is numerically comparable to the plateau of 900–950 mV reported by Suslow (2004) for dilute free-chlorine solutions containing approximately 25 ppm HOCl.



$$E = E^{\circ} - \frac{RT}{2F} \ln \left(\frac{a_{\text{Cl}^-}^2}{a_{\text{Cl}_2}} \right) \quad (3)$$

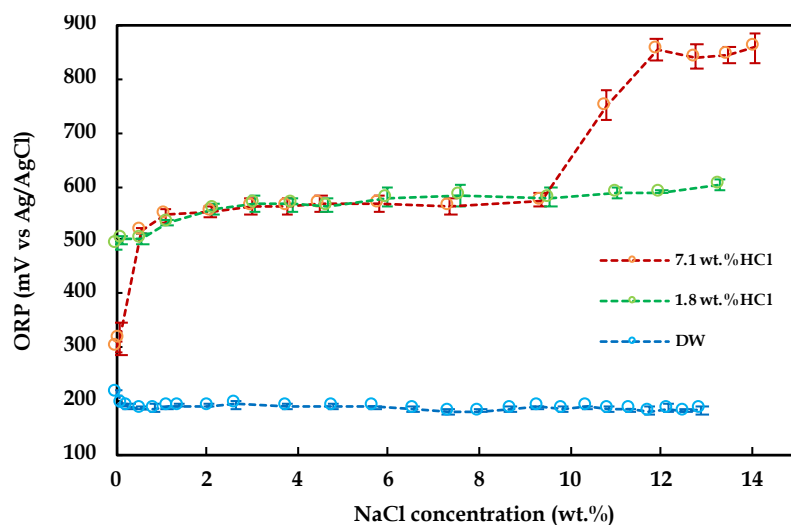
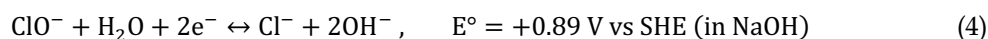


Fig. 4. ORP evolution during incremental NaCl addition under fixed HCl acidity mass fractions, showing a transition from a stabilized moderate ORP to a high-potential regime. Error bars represent the standard deviation of two independent experiments

To evaluate the stability of the high potential regime observed at high chloride concentration, additional experiments were conducted under fixed high-acidity conditions ($\sim 2 \text{ M HCl}$) over a broader NaCl concentration range. The subsequent results, presented in Fig. 5, show that after the transition into the high-ORP regime, the measured potential remained relatively stable near 850–900 mV despite further increases in NaCl concentration. This behaviour suggests the establishment of a buffered oxidizing environment under strongly acidic and chloride-rich conditions. Although some fluctuations were observed at intermediate salinity, the overall ORP remained within the high-potential regime. This behaviour supports the existence of a stable high-potential electrochemical regime in concentrated NaCl-HCl systems.

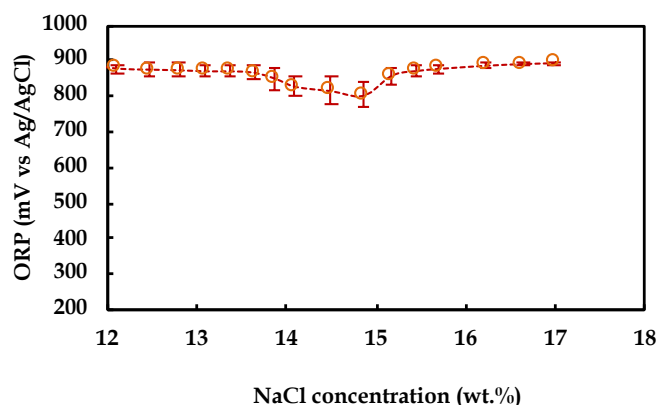


Fig. 5. ORP evolution at elevated NaCl concentration under fixed 7.1 wt.% HCl acidity, showing stabilization of the high-potential regime near 850–900 mV. Error bars represent the standard deviation of two independent experiments

3.2.3. NaCl-HCl systems under fixed salinity conditions and comparison with FeCl_3

In a complementary set of tests, HCl was incrementally added to solutions containing fixed NaCl concentrations to examine the impact of acidification under different salinity backgrounds (Fig. 6). The

results reveal that the presence of NaCl in background shifted the system toward substantially higher and more stable redox potentials compared with HCl-only system. While the distilled-water system reached a maximum ORP of approximately 450 mV before declining toward ~300 mV at higher acid concentrations, both saline systems rapidly increased into a potential regime near 590–620 mV.

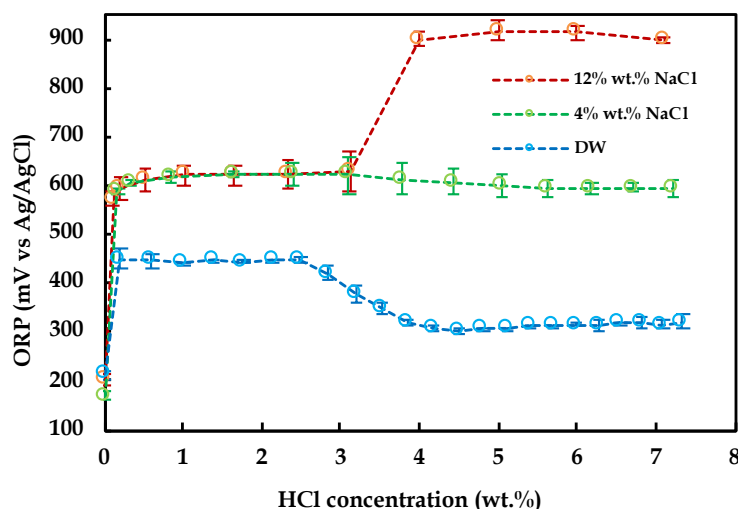


Fig. 6. Effect of NaCl salinity background on ORP evolution during incremental HCl addition. Error bars represent the standard deviation of two independent experiments

In the 4 wt.% NaCl system shown in Fig. 6, ORP increased rapidly during the initial acidification and subsequently stabilized near 590–620 mV despite increasing HCl concentration. At higher salinity, approximately 12 wt.% NaCl, further acidification produced a nonlinear transition toward a high-potential regime approaching 900 mV. Both Fig. 4 and 6 with complementary reagent-addition paths—NaCl addition to a fixed acidic background and HCl addition to a fixed saline background—indicate that both high acidity and chloride concentration are required for the transition to the high-potential regime. This interpretation is further supported by the small-scale experiments in Table 2, where alternative reagent addition sequences at the same NaCl–HCl composition produced comparable ORP values of 903 and 890 mV. Considering the approximate 10 mV readout fluctuation, this difference was not interpreted as significant. The results suggest that development of the high-potential regime depended mainly on the final electrolyte composition rather than on the reagent addition sequence.

Table 2. Assessment of high-potential ORP regime using small-scale (40 mL) single-step experiments under different reagent addition sequences in fixed NaCl–HCl conditions

NaCl, wt.% (approx. g/L)	HCl, wt.% (approx. mol/L)	T (°C)	ORP (mV)	Order
11.5 (≈120)	7.1 (≈2.00)	24	903	DW → NaCl → HCl
11.5 (≈120)	7.1 (≈2.00)	24	890	DW → HCl → NaCl

FeCl₃ as a reference oxidant, was tested in the same experimental approaches to benchmark the ORP response of NaCl–HCl systems against a conventional ferric redox environment. As shown in Fig. 7, both addition sequences produced ORP values mainly within 550–670 mV versus Ag/AgCl. After conversion to the SHE scale, this range is broadly comparable to the standard potential of the Fe³⁺/Fe²⁺ couple ($E^\circ = 0.771$ V vs SHE), although this comparison is only indicative because Fe²⁺ was not controlled. In comparison to concentrated NaCl–HCl system, NaCl is not a consumable oxidant like FeCl₃, but under strongly acidic and chloride-rich conditions it can act as a conditional redox modulator by changing the mixed potential established at the Pt electrode. The analysis also shows that increasing HCl concentrations in FeCl₃ systems results in a small reduction of ORP. This gradual decrease in ORP with increasing HCl may reflect changes in Fe(III) speciation, as stronger chloride complexation and suppressed hydrolysis alter the activity and distribution of ferric species in solution (Persson, 2018; Stefánsson et al., 2019).

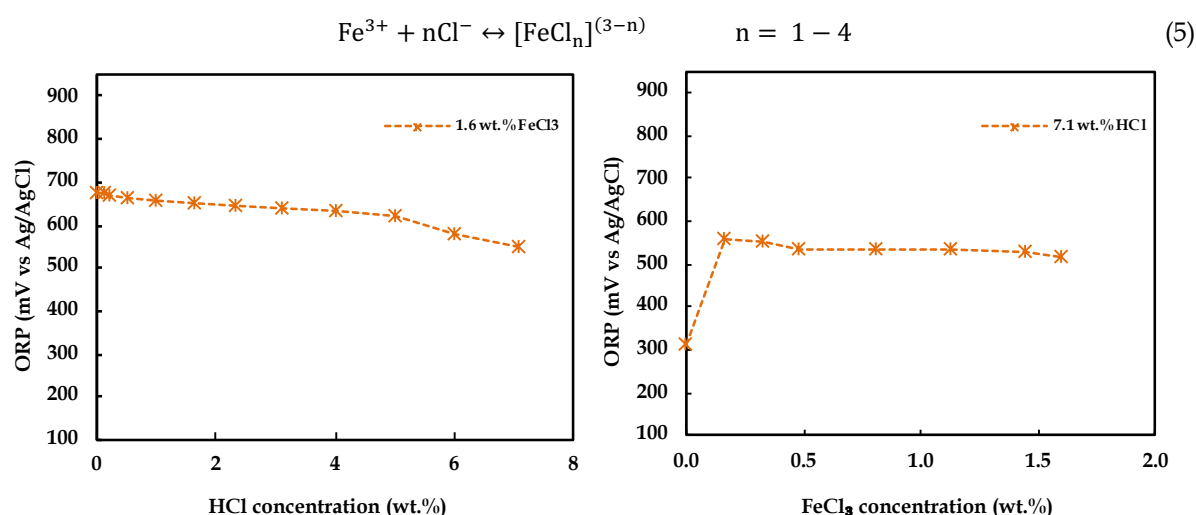


Fig. 7. ORP evolution in acidic ferric chloride systems: (a) ORP response during incremental HCl addition under fixed 1.6 wt.% FeCl_3 (approximately 0.1 M) concentration, (b) ORP response during FeCl_3 addition under fixed 7.1 wt.% HCl (approximately 2.0 M) acidity

3.3. ORP modulation in NaCl - H_2SO_4 systems

The interaction between NaCl concentration and H_2SO_4 acidity on the redox behaviour of the solution was evaluated under different concentration regimes using both fixed-acidity and fixed-salinity experimental approaches.

3.3.1. NaCl addition to H_2SO_4 media with concurrent dilution

The first dataset for NaCl - H_2SO_4 systems is presented in Fig. 8, where NaCl was incrementally added to initially acidified sulfate solutions, resulting in concurrent dilution of sulfuric acid concentration. While the initial acidity levels of 4.8 and 17.5 wt.% H_2SO_4 (approximately 0.5 and 2.0 M, respectively), followed the baseline ORP behaviour discussed in Fig. 1, NaCl results in the absence of acid shows no systematic increase in ORP and remained near 180–200 mV.

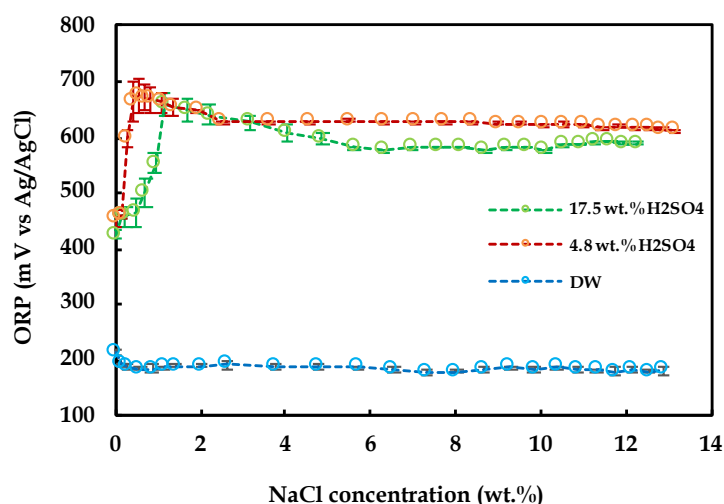


Fig. 8. ORP evolution during incremental NaCl addition into sulfuric acid solutions under fixed initial acidity and progressive acid dilution. Error bars represent the standard deviation of two independent experiments

In both H_2SO_4 concentrations, the initial NaCl addition increased the ORP rapidly to a potential range of approximately 600–670 mV. The main ORP increase occurred up to 1.15 wt.% NaCl for the 2 M H_2SO_4 system (17.5 wt.% H_2SO_4) and 0.55 wt.% NaCl for the lower acidity (4.8 wt.% H_2SO_4 ~0.5 M H_2SO_4) system. Unlike the NaCl -HCl system, no transition to the high-potential regime of

approximately 850–900 mV was observed in NaCl–H₂SO₄ media. This shows that, under the conditions tested, chloride concentration alone was insufficient to produce the high-potential regime and that the acid matrix influenced the mixed potential established at the Pt electrode. Progressive acid dilution, changes in proton activity, increasing ionic strength, and sulfate speciation may have contributed to the plateau near 600 mV, although their individual effects cannot be distinguished from the ORP measurements alone (Stefánsson et al., 2005).

3.3.2. NaCl–H₂SO₄ systems under fixed acidity conditions

To minimize the effect of acid dilution and better isolate the role of NaCl in H₂SO₄ media, a second experimental dataset was collected and plotted in Fig. 9 under a constant mass fraction of acidity background during NaCl addition. Unlike the previous dataset, where NaCl addition progressively diluted the sulfuric acid solution, the acidity mass fraction level was almost maintained throughout the experiment. The results show that, similar to the previous observations, in contrast to distilled water, where ORP remained near 180–200 mV, the addition of NaCl to the both sulfuric acid backgrounds gradually increased the ORP and subsequently stabilized within a range of approximately 580–640 mV at higher NaCl concentrations. This behaviour suggests that the influence of NaCl on ORP becomes significant only in the presence of acid and sufficient proton concentration.

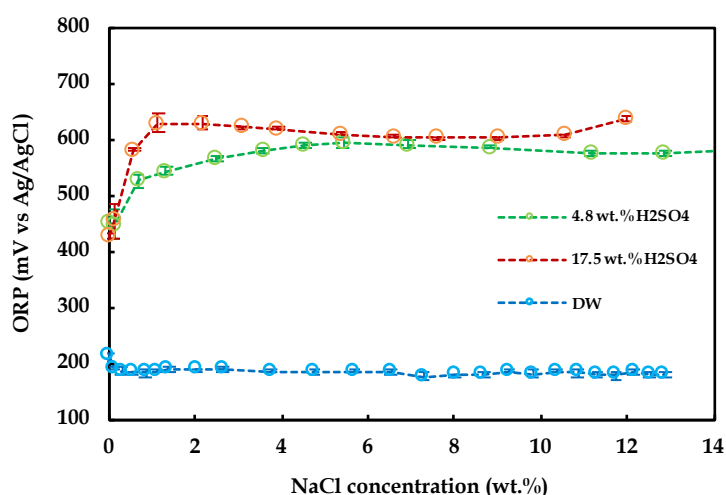


Fig. 9. ORP evolution during incremental NaCl addition under fixed H₂SO₄ acidity conditions, showing the influence of salinity on the redox behavior of sulfate media. Error bars represent the standard deviation of two independent experiments

Under approximately maintained H₂SO₄ acidity, the ORP in the 17.5 wt.% H₂SO₄ system increased from 428 ± 5 to 631 ± 16 mV with the addition of 1.15 wt.% NaCl, whereas the increase in the 4.8 wt.% H₂SO₄ system was more gradual, reaching 594 ± 9 mV at 5.42 wt.% NaCl. At higher NaCl concentrations, both systems entered a moderate-potential region, although the more acidic system generally remained approximately 20 mV higher. As the H₂SO₄ mass fraction was approximately maintained during these experiments, the observed plateau cannot be explained by acid dilution alone and may reflect the combined effects of acidity, ionic strength, and solution speciation on the mixed potential established at the Pt electrode (Stefánsson et al., 2005). Oxygen-related reactions may also contribute, but their role cannot be confirmed because dissolved oxygen was not measured. In neither sulfate system did the ORP approach the 850–900 mV regime observed in concentrated NaCl–HCl media. The absence of a transition toward the high-potential regime (~850–900 mV) highlights the importance of the acid matrix in determining the electrochemical response of saline acidic solutions.

3.3.3. ORP behaviour under fixed salinity conditions and comparison with FeCl₃

A complementary set of experiments, presented in Fig. 10, investigated the effect of H₂SO₄ addition under fixed NaCl salinity backgrounds. Consistent with the baseline results shown in Fig. 1, the addition of H₂SO₄ to distilled water increased ORP, stabilizing the electrochemical environment at

approximately 450 mV. Introducing NaCl as a background electrolyte at both salinity levels of 4 and 12 wt.% NaCl shifted the ORP above that of the salt-free system. This behaviour shows the positive contribution of salinity background on redox potential of acidic systems. Considering that the mean redox potential $\pm$ SD ranges of the two saline systems overlapped across most of the common H_2SO_4 concentration range, increasing the NaCl background from 4 to 12 wt.% did not produce a consistent additional increase in ORP. Instead, both systems established a similar moderate-potential regime, broadly around 600–630 mV, without the high-potential transition observed in the NaCl–HCl system. This suggests that, within the investigated range, the presence of dissolved chloride had a greater influence on the ORP response than increasing its concentration from 4 to 12 wt.%.

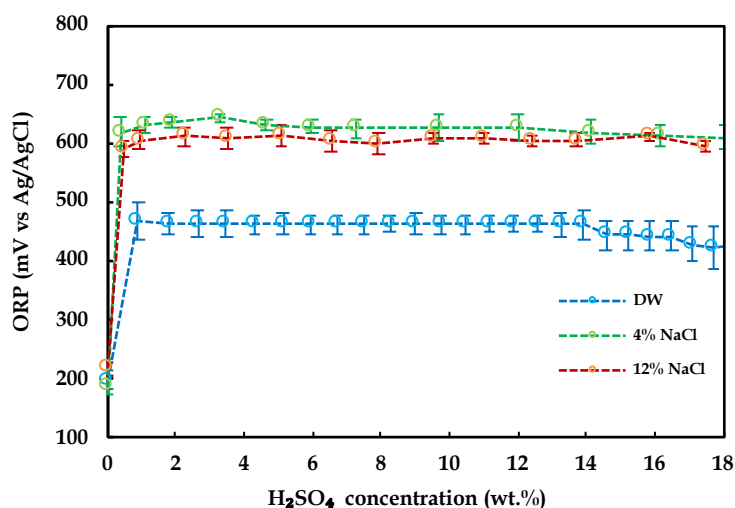


Fig. 10. ORP evolution during incremental H_2SO_4 addition at fixed NaCl backgrounds of 0, 4, and 12 wt.%, showing the effect of dissolved chloride on the redox response of sulfate media. Error bars represent the standard deviation of two independent experiments

FeCl_3 was used as a reference oxidant to compare the stabilized ORP range of NaCl– H_2SO_4 systems with a conventional ferric redox environment. As shown in Fig. 11(a), FeCl_3 addition to 17.5 wt.% H_2SO_4 increased ORP toward the moderate potential range near 600–620 mV, while the presence of 12 wt.% NaCl did not enhance the response. Similarly, Fig. 11(b) shows that NaCl addition to the FeCl_3 – H_2SO_4 background maintained ORP near 600 mV, followed by a slight decrease at higher salinity. These relatively small ORP variations at high chloride concentrations may reflect chloride-induced changes in Fe(III) speciation and effective activity, which can influence the mixed potential measured at the Pt electrode (Persson, 2018; Stefánsson et al., 2019).

Overall, FeCl_3 –sulfate systems exhibited only minor sensitivity to NaCl concentration and the measured potentials were comparable to those typically observed in ferric redox systems ($\text{Fe}^{3+}/\text{Fe}^{2+}$,

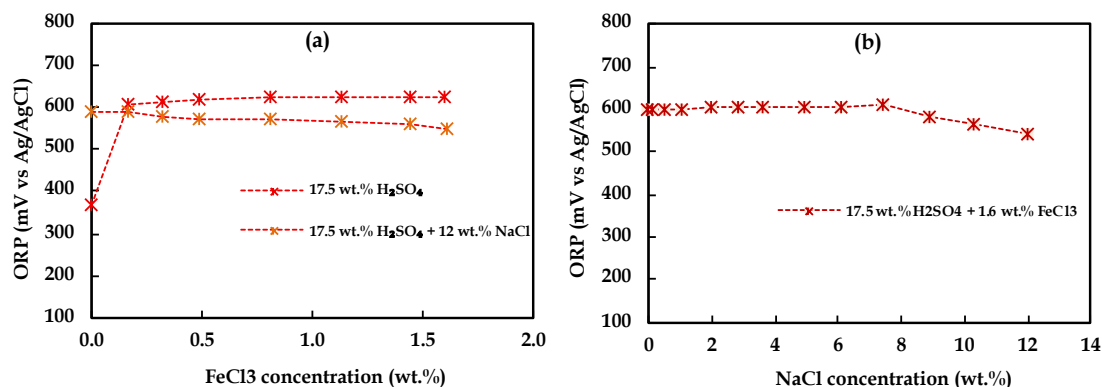


Fig. 11. FeCl_3 reference oxidant response in sulfate media: (a) ORP during FeCl_3 addition to solutions containing 17.5 wt.% H_2SO_4 , with and without 12 wt.% NaCl; and (b) ORP during NaCl addition to a fixed background containing 17.5 wt.% H_2SO_4 and 1.6 wt.% FeCl_3 (approximately 0.1 M)

$E^\circ \approx +0.77$ V vs. SHE). These results suggest that sulfate media remain within a ferric-comparable ORP window, with only limited sensitivity to NaCl concentration under the investigated conditions. It is worth mentioning that, despite temperature increases observed during acid addition, no clear correlation between temperature and ORP was detected. Hence, the measured trends were primarily governed by changes in solution chemistry.

3.4. HCl-H₂SO₄ comparison under matched nominal acid and NaCl conditions

To provide an inferential comparison between the two acid systems, the independently duplicated fixed-acidity series were evaluated at the same nominal analytical acid concentration (approximately 0.5 or 2.0 M). Comparisons were made at the closest experimentally measured NaCl mass fractions in the HCl and H₂SO₄ series. The resulting HCl-H₂SO₄ contrast, expressed as $\Delta\text{ORP} = \text{ORP}(\text{HCl}) - \text{ORP}(\text{H}_2\text{SO}_4)$, is shown in Fig. 12, and the composition-matched inferential results are summarized in Table 3. As both the magnitude and direction of ΔORP changed with NaCl concentration, the comparison was evaluated at individual matched conditions rather than as a single overall HCl-versus-H₂SO₄ effect.

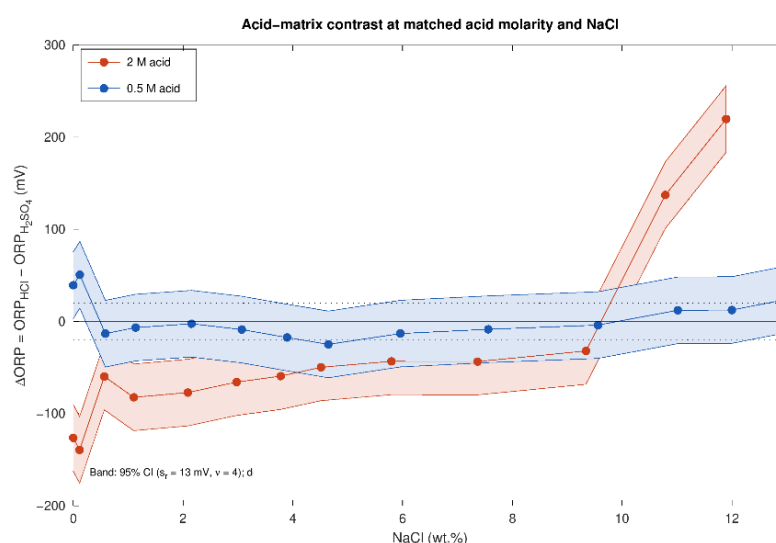


Fig. 12. HCl-H₂SO₄ ORP difference as a function of NaCl concentration at nominal acid concentrations of approximately 0.5 and 2.0 M. The curves provide a graphical representation of the composition-dependent difference between the two systems and the shaded regions show the 95% intervals based on the pooled repeatability SD

At the nominal 2 M acid level, the HCl system showed lower ORP than the H₂SO₄ system at low NaCl concentration. Without NaCl, ΔORP was -126.3 mV, and at approximately 1.1 wt.% NaCl it remained negative at -86.0 mV. These contrasts remained significant after Holm adjustment in the pooled-repeatability analysis (Table 3). The difference decreased at intermediate NaCl concentrations, but a marked change occurred at approximately 12 wt.% NaCl, where the HCl system reached 857.0 ± 19.1 mV compared with 639.5 ± 5.7 mV in the H₂SO₄ system, corresponding to $\Delta\text{ORP} = +217.5$ mV. This reversal is clearly visible in Fig. 12 and is consistent with the high-potential regime observed only in the concentrated HCl system.

At the nominal 0.5 M acid level, the HCl-H₂SO₄ differences were smaller and none of the matched contrasts remained significant after Holm correction. The Welch sensitivity analysis, based on the condition-specific replicate SDs, was more conservative and none of the contrasts remained significant after multiplicity adjustment. This difference between the two variance treatments reflects the limited replication ($n = 2$) and therefore places an important limitation on the strength of the inferential conclusions.

Overall, the comparison indicates that the HCl-H₂SO₄ ORP difference is composition dependent rather than a uniform shift between the two acid systems. However, matching nominal acid concentration and NaCl mass fraction does not produce identical total chloride conditions because HCl

itself contributes chloride whereas H_2SO_4 does not. Therefore, the observed differences reflect the combined influence of acid medium, NaCl concentration and total chloride content.

Table 3. Composition-matched comparison of stabilized ORP between the HCl and H_2SO_4 systems at nominal acid concentrations of approximately 0.5 and 2.0 M

Nominal acid concentration	NaCl, HCl system (wt. %)	ORP, HCl (mean $\pm$ SD, mV)	NaCl, H_2SO_4 system (wt. %)	ORP, H_2SO_4 (mean $\pm$ SD, mV)	ΔORP (mV)	Pointwise 95% CI for ΔORP (mV)	Holm-adjusted P (pooled repeatability)	Holm-adjusted P (Welch sensitivity)
2.0 M	0.00	302.0 $\pm$ 9.9	0.00	428.3 $\pm$ 5.1	-126.3	-162.5 to -90.1	0.0044	0.0950
2.0 M	1.10	545.0 $\pm$ 10.5	1.15	631.0 $\pm$ 15.9	-86.0	-122.2 to -49.8	0.0160	0.2010
2.0 M	5.80	567.0 $\pm$ 16.4	5.37	612.4 $\pm$ 1.7	-45.4	-81.6 to -9.2	0.1260	0.4680
2.0 M	9.34	574.0 $\pm$ 12.3	9.00	605.5 $\pm$ 1.4	-31.5	-67.7 to 4.7	0.2190	0.4680
2.0 M	11.90	857.0 $\pm$ 19.1	12.00	639.5 $\pm$ 5.7	217.5	181.3 to 253.7	0.0006	0.1870
0.5 M	0.00	491.0 $\pm$ 6.9	0.00	451.7 $\pm$ 8.7	39.3	3.1 to 75.5	0.1570	0.2090
0.5 M	5.96	580.0 $\pm$ 19.5	5.42	593.7 $\pm$ 9.3	-13.7	-49.9 to 22.5	0.7050	0.4950
0.5 M	12.00	589.0 $\pm$ 3.3	11.17	577.2 $\pm$ 3.9	11.8	-24.4 to 48.0	0.7050	0.3410

Note: Values are mean $\pm$ SD from two independent runs. $\Delta\text{ORP} = \text{ORP}(\text{HCl}) - \text{ORP}(\text{H}_2\text{SO}_4)$. Reported confidence intervals are pointwise 95% intervals. Holm-adjusted p-values are given for the pooled-repeatability analysis and Welch tests included as a sensitivity analysis

3.5. Time-dependent ORP response, stability, and acid-matrix comparison

As described in the Materials and Methods section, we followed a standardized and uniform method for taking ORP measurements, dedicating sufficient time with continuous mixing to obtain a homogeneous solution and stabilized readings for data acquisition. During the experiments, while ORP was recorded continuously with a sampling interval of 0.5 minutes, high ORP spikes were observed during the acidification of NaCl- H_2SO_4 media at high salinity. Similarly, some thesis research has reported unusually high ORP values in NaCl- H_2SO_4 systems of comparable concentration and composition (Cubarol 2024).

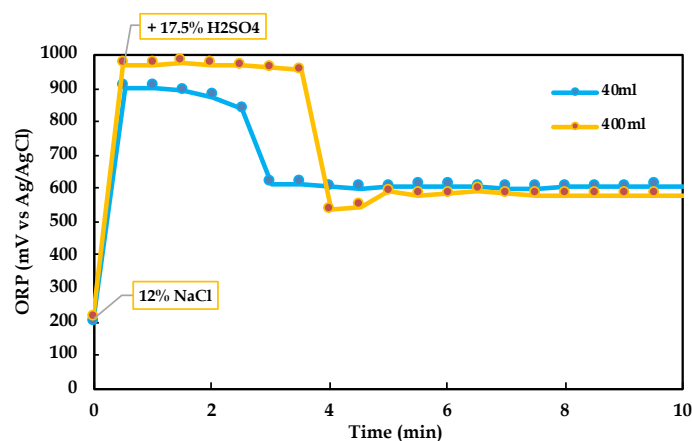


Fig. 13. Dynamic ORP response following acidification of a 12 wt. % NaCl solution to approximately 2 M H_2SO_4 . Measurements were performed at two solution scales (40 and 400 mL)

Dynamic ORP measurements were performed at two solution scales (40 mL and 400 mL) to determine whether these elevated potentials represented a stable redox state. Following acidification of a 12 wt.% NaCl solution to approximately 2 M H_2SO_4 , ORP increased sharply to approximately 900–970 mV within the first minute. As shown in the time dependent redox potential profile of this system in Fig. 13, the elevated potentials were followed by a rapid decline toward a stable ORP range of approximately 580–610 mV within a few minutes. This behaviour cannot simply indicate the bulk thermodynamic redox state but rather may reflect transient and non-equilibrium occurring during acidification and mixing (Rabenhorst et al., 2009).

Under the same experimental setting, time-dependent measurements were also examined for the high potential NaCl–HCl systems containing approximately 7.1 wt.% HCl and 12 wt.% NaCl. Unlike the transient response observed in the NaCl– H_2SO_4 system, the NaCl–HCl response in Fig. 14 at both 40 and 400 mL systems, remained almost within the high-potential range throughout the monitored period. At approximately 7.1 wt.% HCl and 12 wt.% NaCl, ORP remained within 897.4–903.7 mV in the 40 mL system and within 890.5–893.0 mV in the 400 mL system from 3 min onward. These profiles support that the reported values were obtained from the stabilized part of the response rather than from the initial transition following reagent addition. According to fundamental ORP measurement principles, as the solution becomes homogeneous and the diffusion layers around the electrode equilibrate, the measured potential stabilizes at a value that is more representative of the steady-state redox environment (Suslow, 2004). The time dependent behaviour of the two acid systems highlights the importance of applying a standardized stabilization protocol. Considering that ORP electrodes require time to equilibrate with changes in solution chemistry, all relevant measurements in this research were recorded only after allowing sufficient time for stabilization.

Although both time-dependent experiments contained approximately 12 wt.% NaCl, the total chloride content of the two systems was different because HCl also contributes chloride ions. Based on the nominal solution compositions summarized in Table 4, the system containing 7.1 wt.% HCl and 12 wt.% NaCl had a total chloride content of approximately 14.2 wt.%. In comparison, the NaCl– H_2SO_4

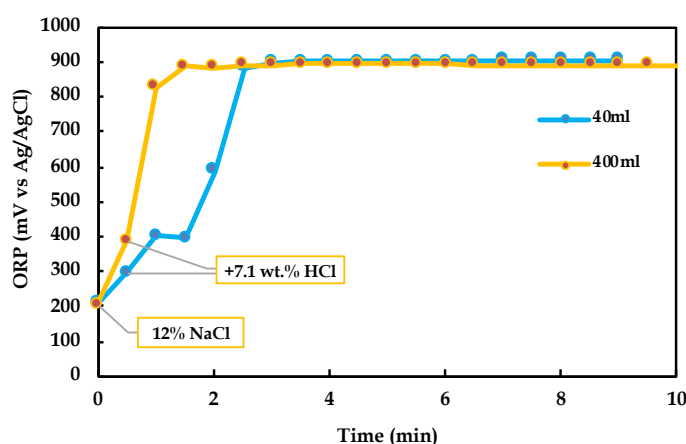


Fig. 14. Dynamic ORP response following acidification of a 12 wt.% NaCl solution to approximately 2 M HCl. Measurements were performed at two solution scales (40 and 400 mL)

Table 4. Comparison of nominal chloride content and stabilized ORP observed in time-dependent experiments conducted at 40 and 400 mL scales in NaCl–HCl and NaCl– H_2SO_4 systems.

System	Cl^- from NaCl (wt.%)	Cl^- from acid (wt.%)	Total nominal Cl^- (wt.%)	Relative chloride content	Stabilized ORP (mV)
7.1 wt.% HCl + 12 wt.% NaCl	7.28	6.90	14.18	1.95	≈890–900
17.5 wt.% H_2SO_4 + 12 wt.% NaCl	7.28	0	7.28	1.00	≈580–610

system contained approximately 7.28 wt.% Cl^- , supplied only by NaCl. Thus, the nominal chloride content of the NaCl-HCl system was nearly twice that of the NaCl-H₂SO₄ system. This higher chloride content is considered an important compositional factor that may contribute to the different ORP behaviour observed in the two acid systems.

3.6. Thermodynamic interpretation of ORP regimes

A thermodynamic context for the measured ORP regimes was provided using Cl-H₂O Pourbaix diagrams constructed at total chloride concentrations of 1 and 4 using HSC Chemistry and literature data (Fig. 15). For comparison with the thermodynamic stability domains, the measured potentials were approximately converted from the Ag/AgCl scale to the SHE scale using $E_h(\text{SHE}) = \text{ORP}(\text{Ag}/\text{AgCl}) + 0.197\text{--}0.210\text{ V}$. A reference potential range of +0.197 to +0.210 V at 25 °C was considered for the Ag/AgCl electrode, corresponding to concentrated-KCl reference systems.

The moderate-potential regime of approximately 550–620 mV versus Ag/AgCl, corresponding to about 0.75–0.83 V versus SHE, was observed in both NaCl-HCl and NaCl-H₂SO₄ systems. In contrast, the high-potential regime of approximately 850–900 mV versus Ag/AgCl, or about 1.05–1.11 V versus SHE, developed only in strongly acidic NaCl-HCl solutions containing high NaCl concentrations. This distinction is noteworthy because NaCl-H₂SO₄ can reach similarly low, and in some tests even lower pH than NaCl-HCl, but it remains in a moderate ORP window. From the point of chloride availability, HCl contributes additional chloride ions together with NaCl, unlike H₂SO₄. The greater total chloride availability in concentrated NaCl-HCl solutions may contribute to the observed high-potential response. This suggests that the greater total chloride input could favour chloride-related oxidation pathways. However, since chlorine-containing species were not directly analysed, this interpretation remains tentative. In addition, the response cannot be attributed to chloride concentration alone, as NaCl without strong acidity did not produce a comparable increase in ORP as shown by experiments of NaCl addition to distilled water with ORP values near 180–200 mV (Fig. 1). All these observations indicate that neither proton nor chloride concentration alone can lead to the observed ORP response (Héduit and Thévenot, 1992). Furthermore, because NaCl was the only chloride salt investigated in this study, possible cation-specific effects are not separated from the chloride contribution.

Comparing our measurements with the Cl-H₂O Pourbaix diagrams in Fig. 15 shows that the experimental Pt/Ag/AgCl potentials, converted to the SHE scale, do not coincide directly with the equilibrium potentials of either the O₂/H₂O or Cl₂/Cl⁻ equilibrium boundaries under the assumed conditions. The measured values remain largely within the water-stability region and the chloride stability field. This difference is expected because Pourbaix diagrams represent equilibrium stability domains, whereas a Pt/Ag/AgCl electrode in a solution containing several possible interfacial reactions measures a mixed potential rather than a unique equilibrium Eh (Héduit and Thévenot, 1992; Stefánsson et al., 2005). Moreover, because the investigated solutions are highly concentrated, analytical concentrations cannot be assumed to represent thermodynamic activities directly. To determine whether solution non-ideality could affect the thermodynamic comparison, the equilibrium boundaries were recalculated for the fixed 7.1 wt.% HCl-NaCl series, where the transition to the high-potential regime was observed. Fig. 16 compares the molality-based boundaries calculated assuming unit activity coefficients with the corresponding boundaries obtained using Pitzer-model-derived activities. The activity correction shifted both equilibrium boundaries, but the effect was smaller for the Cl₂(g)/Cl⁻ boundary than for the O₂/H₂O boundary, which showed a clearer composition-dependent shift as NaCl concentration increased. Nevertheless, both activity-corrected boundaries remained above the measured Pt-electrode potentials throughout the investigated NaCl range, including the high-potential regime. Therefore, including solution non-ideality in the thermodynamic analysis shifts the equilibrium reference lines but does not change their overall position relative to the experimental ORP. This is consistent with the interpretation of the measured response as a mixed Pt-electrode potential rather than the equilibrium potential of individual redox couple.

In our experiments, although the measured potentials remained within the chloride stability field in Cl-H₂O Pourbaix diagrams (Fig. 15), the high-potential regime observed in the NaCl-HCl systems under strongly acidic and chloride conditions can be discussed, as a working hypothesis of a stronger chloride-dependent interfacial contribution. Since the measured potentials did not reach the Pourbaix

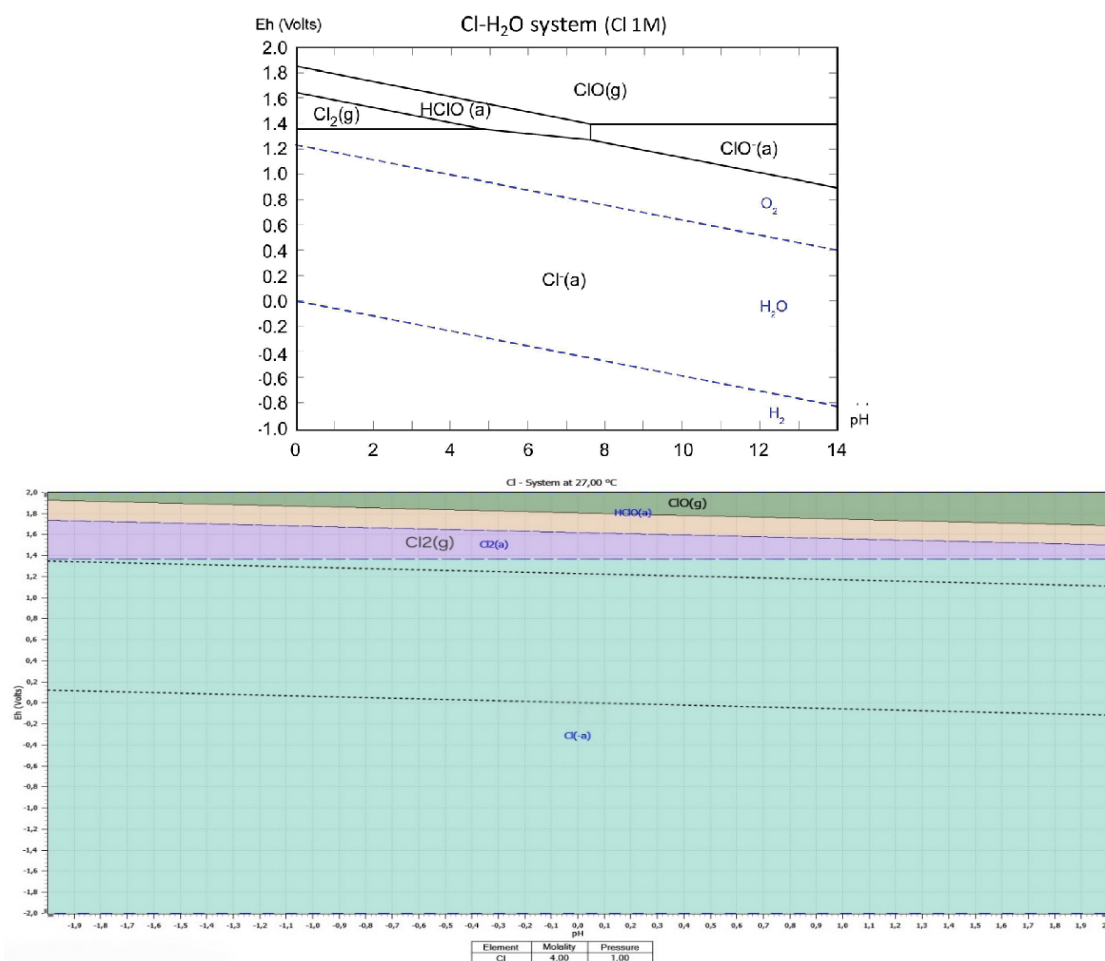


Fig. 15. Cl-H₂O Pourbaix diagrams used to contextualize the experimentally observed ORP regimes. (a) Cl-H₂O diagram adapted from Radepon et al. (2015) over the pH range 0–14. (b) Cl-H₂O diagram generated using HSC Chemistry at 27 °C and 4 chloride molarity over the acidic pH range in the NaCl-HCl and NaCl-H₂SO₄ systems (–2 to 2)

stability domains of active chlorine species and because Cl₂ and HOCl were not measured, the high ORP does not provide evidence for the formation of active chlorine species in the solution. Even so, the results suggest that chloride has a stronger influence on the mixed potential established at the Pt electrode. Therefore, a chloride-related interfacial contribution is possible, as chloride oxidation on Pt has been shown to be kinetically feasible in concentrated NaCl solutions under anodic polarization (Patil et al., 2011), although those conditions differ from the open-circuit measurements used here. In the moderate-potential regime observed in both NaCl-HCl and NaCl-H₂SO₄ systems, dissolved oxygen may represent another possible contribution at the Pt surface. However, dissolved oxygen was not measured so it cannot be identified as the controlling process. Chloride adsorption has been reported to modify oxygen-reduction kinetics on Pt, therefore it may shift the measured potential by changing the interfacial reaction kinetics (Schmidt et al., 2001). Studies using Pt electrodes also show that dissolved oxygen can contribute to a mixed potential involving simultaneous interfacial reactions (Zimmermann et al., 2018). Consequently, the Pourbaix analysis is used only to place the experimental potentials relative to the equilibrium stability domains not as direct proof of chlorine generation or O₂/H₂O equilibrium.

4. Conclusions

This study examined the influence of NaCl concentration on the measured oxidation–reduction potential behaviour in two acidic media, H₂SO₄ and HCl, extending the interpretation of NaCl beyond its commonly discussed role in promoting surface depassivation in leaching systems. The results show

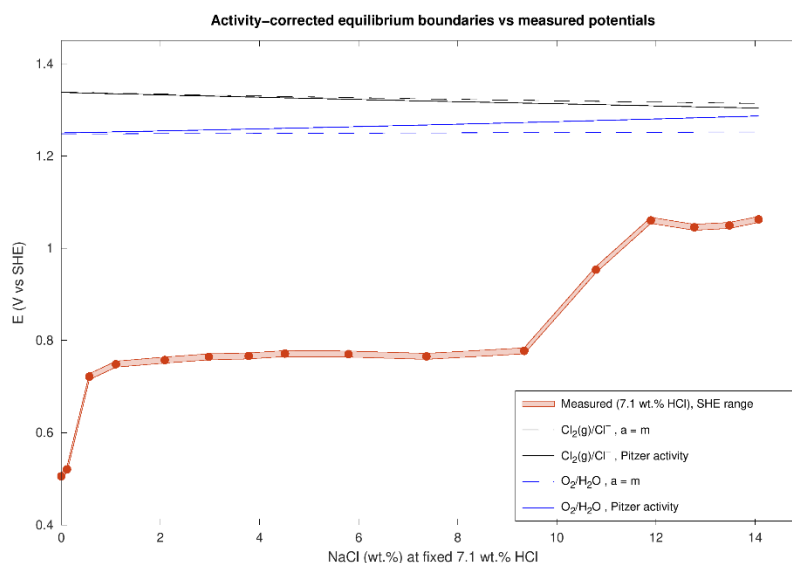


Fig. 16. Measured ORP and molality-based versus Pitzer activity-corrected $\text{Cl}_2(\text{g})/\text{Cl}^-$ and $\text{O}_2/\text{H}_2\text{O}$ equilibrium boundaries for the fixed 7.1 wt.% HCl–NaCl series at 25 °C. Dashed lines represent boundaries calculated by approximating activity with molality ($a = m$)

that the effect of NaCl on solution redox potential depends strongly on the acid matrix and cannot be explained solely by chloride concentration or proton activity. In this research, the importance of standardized stabilization procedures was highlighted by continuous ORP measurements to have a reliable interpretation of solution redox behaviour. These measurements showed that transient potentials approaching 900–970 mV can occur once acid is added to high-salinity sulfate systems, but they rapidly decrease toward a stable ORP near 600 mV. Thus, the interpretation of redox behaviour should be based on equilibrated measurements not transient electrode responses.

In NaCl–HCl systems, increasing salinity in highly acidic conditions increased the redox potential from a moderate ORP range of approximately 550–620 mV to a high-potential regime approaching 850–900 mV (Ag/AgCl). In NaCl– H_2SO_4 systems, the redox potential remained within a stable moderate window of approximately 580–640 mV (Ag/AgCl). Comparative analysis demonstrated that neither proton activity nor NaCl concentration alone can explain the observed ORP enhancement. The NaCl–HCl experiments contained substantially higher total chloride content than the corresponding NaCl– H_2SO_4 experiments because HCl also contributes chloride ions. Therefore, both total chloride content and acid matrix should be considered when comparing the two systems. It is also important to consider that the measured response is a mixed potential at the platinum electrode, which reflects the combined influence of the acid medium and the redox-active species present, rather than the equilibrium potential of a single redox couple.

Comparison of the experimental data with Cl– H_2O Pourbaix diagrams showed that the measured ORP values remained within the water-stability region and did not coincide directly with the equilibrium boundaries of the $\text{O}_2/\text{H}_2\text{O}$ or Cl_2/Cl^- couples. The Pourbaix diagrams are therefore considered a thermodynamic reference rather than a direct predictor of the measured potential. The appearance of the high-potential regime only in NaCl–HCl systems suggest a greater chloride-related contribution under strongly acidic conditions; however, the specific contribution of chlorine-containing oxidizing species could not be confirmed because these species were not directly measured.

Overall, the findings show that the role of NaCl may extend beyond the mineral-surface phenomena commonly discussed in chloride-assisted leaching, as it can also modify the electrochemical environment of the leachate solution itself. These findings suggest that ORP modulation may be a relevant factor when interpreting NaCl-containing hydrometallurgical systems. However, the direct effects of the observed ORP changes on leaching performance and process efficiency were not quantified in the present study; so their industrial impact cannot yet be quantified. Future studies on ORP measurements with dissolved oxygen monitoring, chlorine-species analysis and leaching performance evaluation would provide a better understanding of the relationship between solution chemistry,

mixed-potential behaviour and metal dissolution in chloride-assisted hydrometallurgical systems. Since NaCl was the only chloride and salinity source investigated in this study, comparative experiments using KCl at equivalent chloride concentrations are also recommended to distinguish chloride related effects from possible cation specific contributions.

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