Examining Ni-laterite leach mineralogy & chemistry – a holistic multi-scale approach

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ABSTRACT
Ambient acid leach extraction of Ni-laterites is being heralded as a breakthrough in environmentally conscious mining, however to be successfully exploited they require comprehensive characterisation of their mineralogy and chemistry. This industry-academia collaborative research uses XRD, EPMA and ICPAES techniques to examine the acid leaching characteristics of Turkish Çaldag ore. Mineral scale and small column scale leach experiments were carried out with material examined over various lengths of time at ambient conditions. The characterised residues and solution leach inter-relationships and selectivities are compared to bottle roll and heap leach results, demonstrating where true correlations exist and where differences exist as a result of the experimental scale limitations.

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1. Introduction

Ambient acid leach extraction of Ni-laterites is being heralded as a breakthrough in environmentally conscious mining. Of the total land-based global Ni resources more than 70% are lateritic in nature (Berger et al., 2011; Davidson, 2006) yet currently they account for only ~40% of the annual global production, with this production likely to increase in the coming years as the alternative Ni-sulphide reserves are exploited and decline. Given the low-carbon footprint, low energy consumption, simple equipment technology and low capital costs needed for atmospheric heap leaching (McDonald and Whittington, 2008; Norgate and Jahanshahi, 2011), as compared to high pressure acid leaching (HPAL), bioleaching or (hydro-)pyrometallurgy, it is responsible to consider this metallurgical processing route as a viable alternative to more traditional methods.

Compared to other heap leaching technologies (notably copper and gold) ambient acid leaching of Ni-laterites is in its infancy, and as such there is little published literature specifically examining the reactions occurring during leaching. To date much of the industry knowledge and know-how is contained within confidential internal reports, derived from demonstration-scale test facilities, nevertheless Watling et al. (2011) comprehensively summarise the issues and challenges (including variable ore mineralogy) of heap leaching Ni-laterites, and Castro et al. (2009) have attempted to semi-quantitatively evaluate nickel extraction with respect to its host mineralogy.

The Çaldag Ni-laterite deposit in western Anatolia (Turkey) has a JORC proven resource of 33.2 million tonnes with an average grade of 1.14% Ni and 0.07% Co and was an early demonstration scale example (Oxley et al., 2006a-c) of the application of atmospheric heap leach extraction technology to Ni-laterites. It has been shown (Thorne et al., 2009) to have developed on an ophiolitic serpentinite body obducted onto Triassic dolomites. Geologically it is dominated by a goethite-rich limonitic zone, the main ore body, with a hematite horizon above, which is overlain by freshwater limestones (carbonates) or a siliceous cap. Little saprolite is present such that the limonite often sits directly on top of the largely unweathered serpentinite protolith (bedrock).

This study examines the ambient-temperature dilute sulphuric acid leaching characteristics of Çaldag’s nickeliferous limonite at a variety of scales, with a view to identifying correlated leaching relationships within the extracted elements.

2. Experimental

2.1. Samples and methods

Fresh ore samples, representative of the average Çaldag ore composition, were fully characterised before ambient acid leaching was undertaken. Leaching was performed at a variety of scales with a view to examining the element leaching relationships (not %extraction):
(a) Mineral grain scale: 1.0 g representative sub-samples of limonite were taken and placed in individually labelled tubes. 45 ml DI water was added to one sample tube, to act as a control, whilst the others received 45 ml of 75 g\(^{-1}\) \(\text{H}_2\text{SO}_4\) solution (20.38 ml conc. \(\text{H}_2\text{SO}_4\) diluted to 500 ml with DI water). These tubes were capped and placed on a rotating/shaking table at room temperature for differing lengths of time (2, 7, 24, 35, 57, 72 and 91 days). The tubes were removed periodically, and centrifuged at up to 9000 rpm for 10 min to separate the acid–washed solid from the supernatant liquor. The supernatant solution was subsequently analysed by ICPAES, whilst the solid was dried at <100 °C and both (i) powdered for XRD examination and (ii) prepared as polished resin blocks prior to electron microprobe study for signs of compositional alteration to the ore particles as a result of the acid washing.

(b) Bottle-roll scale: 150 g of finely powdered limonite were placed in a labelled bottle which received 1500 ml of 75 g\(^{-1}\) \(\text{H}_2\text{SO}_4\) solution. The sealed bottle was placed on a test system rotating at a constant 7 rpm at ambient temperature; its solution was maintained at 75 g\(^{-1}\) throughout the test and analysed regularly for Fe, Ni and Co concentrations. Variations in Co concentrations were quantified for signs of compositional alteration to the ore particles as a result of the acid washing.

(c) Small column scale: Seven 1 m \(\times\) 100 mm i.d. Perspex columns were leak tested before being filled with ~8.6 kg representative limonite (~90 cm height) and irrigated using 60 g\(^{-1}\) \(\text{H}_2\text{SO}_4\) solution from a single feed drum in closed circuit mode at room temperature. Each column, underflow container and the feed drum was loosely capped to act as a control, whilst the others received 45 ml of 75 g\(^{-1}\) \(\text{H}_2\text{SO}_4\) solution. The sealed bottle was placed on a test system rotating at a constant 7 rpm at ambient temperature; its solution was maintained at 75 g\(^{-1}\) throughout the test and analysed regularly for Fe, Ni and Co concentrations over a 90 day period. Two sets of bottle roll results are presented to illustrate limonite leach variations.

(d) 4 m heap scale: A heap containing 4318 tonnes of dry limonite was built to a height of 4 m with a 1240 m\(^2\) footprint. Under ambient conditions this heap was irrigated via a trickle irrigation system using ~60 g\(^{-1}\) dilute \(\text{H}_2\text{SO}_4\) solution at a 5.0 lm\(^{-1}\) h\(^{-1}\) target irrigation rate. Evaporation monitoring occurred concurrently and is taken into account in the metallurgical data presented. As such this is an appropriate demonstration scale dataset with which to make meaningful comparative-scale analyses.

2.2. Instrumentation details

Unless stated otherwise all the characterisation was performed on instruments at the Natural History Museum, London.

X-ray powder diffraction (XRD) data were collected using a Nonius PDS120 Powder Diffraction System with an INEL curved position sensitive detector (PSD). Copper K\(\alpha_1\) radiation was selected from the primary beam using a germanium 111 single-crystal monochromator; NIST silicon powder SRM640 and silver behenate were used as external 2\(\theta\) calibration standards. Each sample was ground to a fine powder before being analysed. The mineral phases were identified by search-match procedures using STOE WinXPOW software containing the Powder Diffraction File PDF-2 supplied by the International Centre for Diffraction Data (ICDD).

Inductively coupled plasma atomic emission spectrometry (ICPAES) analyses were collected on a Varian VISTA PRO ICP-AES instrument. The unfiltered leach liquors were appropriately

Fig. 1. Optical images of hand-picked grains: (a) fresh ore blue-green coloured, disordered, mixed layer kaolinite–smectite fragment with orange–brown goethite coating, (b) fresh ore cream coloured grain of calcite with associated silicates, (c) gypsum-coated dolomite particle (soft colourless rim surrounding hard off-white/grey coloured core), recovered from the small column experiment after leaching and (d) dark magnetic flecks contained within an off-white quartz matrix, recovered from the small column experiment after leaching; scale bar = 1 mm. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
luted, with the data calibrated and interpreted using the Varian ICP Expert software, version 4.1.0. Trace element analysis was performed on a Varian ICP-MS instrument. The fresh raw ore results were obtained by means of a lithium metaborate fusion and hydrofluoric/perchloric acid dissolution prior to analysis. Analysis of the 4 m heap solutions, by ICPAES, and the bottle roll solutions (Fe, Ni and Co by atomic absorption spectrometry) were outsourced to commercial laboratories.

Polished resin-mounted blocks were prepared for the fresh ore and selected acid-leached residues. The samples were examined by electron probe microanalysis (EPMA) using either a Cameca SX-50 or a Cameca SX100 instrument, operating at 20 kV, 20 nA and 1 μm spot size for point analyses or 20 kV, 60 nA and 1 μm spot size in mapping mode. These EPMA instruments were fitted with wavelength dispersive X-ray crystal spectrometers (WDS analysis) able to operate in both quantitative analytical (quantitative point analysis) and X-ray mapping mode which produces maps showing the relative concentrations of elements of interest.

3. Results and discussion

3.1. Mineralogy overview

The Çaldag Ni-laterite ore consists of particles or grains which are all composite in nature. Goethite and quartz are the dominant mineral phases identified by XRD in the bulk powder, however they do not convey the real complexity of the mineralogy contained within the Çaldag ore. To this end individual mineral grains were also hand-picked and examined by XRD. They show that a range of silicates are present including (pale) green lizardite, Fe-rich clinohlorite, muscovite (mica), talc and some intensely blue-green coloured kaolinite–smectite (clay) minerals, Fig. 1. Furthermore some particles of pure calcite CaCO₃ have been identified; it is known (Thorne et al., 2009) that calcite veins run through the deposit, whilst the whole deposit sits upon Triassic dolomites. Hard, yet brittle, darker brown laterites. Reassuringly Fe and Si are the dominant elements present, with Fe mainly found in the goethite phase and as cationic substitutions within silicate minerals, whilst Si exists in the goethite particles, the silicates and in quartz. It is likely that much of the Ca is contained within the calcite and dolomite phases. Mg is hosted within the dolomite and the layered silicates lizardite, clinohlorite, saponite and talc. Given that Mg and Ni have similar ionic radii, Ni will readily substitute for Mg in many structures.

The chemical composition of the Çaldag ore has been determined, Table 1. This range reflects the natural heterogeneity of the ore at a mineral grain scale, an intrinsic property of Ni-laterites. Reassuringly Fe and Si are the dominant elements present, with Fe mainly found in the goethite phase and as cationic substitutions within silicate minerals, whilst Si exists in the goethite particles, the silicates and in quartz. It is likely that much of the Ca is contained within the calcite and dolomite phases. Mg is hosted within the dolomite and the layered silicates lizardite, clinohlorite, saponite and talc. Given that Mg and Ni have similar ionic radii, Ni will readily substitute for Mg in many structures. Additionally Ni is present in the goethite phase, Fig. 2, suggesting that it has a number of mineral hosts within this ore. The Al³⁺ ion will also substitute into goethite, in addition to the layered silicate materials. Meanwhile, the transition metals Cr and Mn can exist with variable oxidation states and coordination geometries and as such can substitute within many structures, particularly the clay minerals, and are often major elements within the identified acid-resistant spinels. Finally the presence of S in the fresh ore is intriguing; no specific sulphur-containing phases were identified in the hand-picked grains however gypsum (CaSO₄·2H₂O) is common in the upper parts of the limonite zone at the Çaldag deposit and therefore could contribute to the S value obtained. No specific Co hosts were identified by XRD, nevertheless X-ray element mapping shows that discrete Mn-oxide asbolane grains, which can host Co, are present, Fig. 2a, and Co may also be accommodated within goethite.

3.2. Characterisation – goethite particles

Examining the orange-brown goethite particles in detail illustrates how this Ni-hosting mineral responds to ambient leaching with dilute H₂SO₄. The fresh ore goethite grains, Fig. 2a, are similar to many others investigated and show relatively homogeneous Ni and Fe distribution throughout. Sulphur levels are negligible, confirming that there is little sulphate component associated with the fresh limonitic goethite. Overall there is only limited variation in Ni (2.24 ± 0.08 w.t%) whilst the Fe content varies commensurately, at around 48.0 ± 1.5 w.t%.

Initial leaching of the limonitic ore for 2 days in the mineral grain scale experiments gives an indication of the processes occurring within the neutralisation stage of any ambient leach process. Significantly the goethite particles now show variable distribution of sulphur, indicative of the partial ingress of sulphuric acid into the grain, Fig. 2b. Thus the highest S values are coincident with both Fe and Ni lows, suggesting that Fe and Ni have been leached into solution. This effect is particularly apparent at point 15, the probable site of a crack along which acid could pass more easily. The map for Si is indicative of slight silicification in the goethite around the margins and in cavities.

Extending the mineral grain scale leach time to 35 days results in goethite particles of distinctly ‘porous’ appearance, Fig. 2c. Microprobe analyses confirm that the average Ni content of such goethite grains has decreased to <1 w.t% whilst the Fe levels across the line scan show some co-incident and very distinct zones of depletion. Furthermore the S map suggests complete enrichment such that acid ingress into the goethite grain has created distinct S-rich zones around the grain extremities and as clusters in fractures and cavities. This enrichment suggests the formation of a discrete S-bearing phase (a secondary sulphate phase, perhaps of the jarosite–alunite {KFe₃(SO₄)₂(OH)₆−KAl₃(SO₄)₂(OH)₆} group of min-

| Table 1 Chemical compositional range for the fresh Çaldag limonite ore (wt% element). | LoD = ‘limit of detection’, < indicates signal is below the LoD. |
|--------------|--------|---------|---------|
| Wt% LoD Lower limit Upper limit | Wt% LoD Lower limit Upper limit |
| Al 0.0025 2.1382 2.1842 | As 0.0020 < 0.0425 |
| Ba 0.0020 0.0114 0.0160 | Ca 0.0350 0.8791 1.3715 |
| Cd 0.0001 < < | Co 0.0030 0.0603 0.0884 |
| Cr 0.0100 0.7844 0.9458 | Cu 0.0040 0.0054 0.0070 |
| Fe 0.0055 27.5507 31.6913 | K 0.0040 < 0.2103 |
| Li 0.0005 0.0010 0.0017 | Mg 0.0600 0.7490 1.3791 |
| Mn 0.0030 0.2537 0.3391 | Na 0.0040 < 0.0945 |
| Ni 0.0200 1.1086 1.4820 | P 0.0020 < 0.0188 |
| Pb 0.0020 < < | Rb 0.0020 < < |
| S 0.0040 0.0897 0.1450 | Sc 0.0005 0.0044 0.0044 |
| Si 0.0500 11.6439 19.2211 | Sr 0.0005 0.0023 0.0046 |
| Ti 0.0060 0.0541 0.0764 | V 0.0020 < 0.0113 |
| Y 0.0001 0.0006 0.0007 | Zn 0.0005 0.0245 0.0449 |
| Zr 0.0150 < 0.0014 | 0.0014 |
erals) rather than simple sulphate diffusion into the goethite matrix.

After 72 days ambient leaching at the mineral grain scale the average porous relic goethite fragment has a ~30 wt% Fe and 0.4 wt% Ni content, confirming that acid dissolution of goethite is effective. This is further confirmed by the paucity of residual goethite grains identified at this scale, with ubiquitous S enrichment across the few remaining goethite particles. Overall it is calculated that the goethite may still retain at least 30% of the original Ni, indicating that long-term leaching (and complete goethite dissolution) is needed for full liberation. Reassuringly washing in DI water for 72 days (the control) identified no mineralogical changes, with negligible metal extraction into solution.

3.3. Characterisation – associated minerals

Although goethite and quartz dominate the mineralogy of the Çaldag ore a number of the other more minor minerals play important roles in the overall metallurgical extraction story.

On occasion very Ni-rich grains are present in the fresh ore, Fig. 2a. These also contain elevated Mn and Co, indicative of the presence of nickeliferous asbolane ([CoNi]Mn2O4(OH)2·nH2O), and may be a minor but significant repository of Ni. Asbolane is amenable to ambient temperature leaching and is not identified in any subsequent X-ray mapped grains.

Often a silicified rim around and/or a siliceous matrix throughout the goethite particles is identified. This is likely to be due to a combination of Fe3+/Fe2+ charge transfer and/or incorporation of trace amounts of other highly coloured dopant ions (e.g. Cr, Mn) within the crystal structures of nonexpandable phyllosilicates. The inclusion of trace amounts of dopant ions, not detectable by XRD, will contribute to the leached solution composition following acid attack on their mineral host.

Spinel group minerals, particularly chromite and maghemite, in addition to hematite grains are present in minor/trace amounts throughout the ore, and are characteristically acid resistant when compared to goethite. These Fe hosts are able to take up minor/trace amounts of other elements (including Ni, Mn and Cr) releasing them gradually, presumably as a function of their surface area.

The fresh ore contains discrete fragments of calcite CaCO3 and dolomite CaMg(CO3)2. The identification of soft, colourless, fine grained, Ca-sulphate species surrounding dolomite grains, contained within the leached residues, is shown in Fig. 1. Coupled with the absence of calcite particles in the leached residues, it suggests that on first contact the dilute H2SO4 acid (a strong acid) used for leaching both attacks and completely dissolves any calcite present and selectively leaches magnesium (Mg2+) from dolomite. Consequently as acid leaching progresses the surfaces of the relic dolo-

**Fig. 2.** Selected X-ray element maps for goethite particles after ambient temperature acid leaching for: (a) 0 days (i.e. fresh ore), (b) 2 days and (c) 35 days at the mineral grain scale. Marked in white on selected maps is the position of the quantitative line scan shown to the far right hand side where Ni and S data are plotted on the secondary axes; a Mn-oxide grain is highlighted in the Co map; scale bar = 100 μm.
mite grains become enriched in calcium, which when combined with sulphate anions from the acidic leach liquor under the favourable (local super-saturation) conditions will instantly precipitate as a new Ca-sulphate phase (most likely as gypsum CaSO\textsubscript{4}-2H\textsubscript{2}O). Despite there being no structural (epitaxial) reason for Ca-sulphate species to grow on dolomite surfaces it is envisaged that a reaction front forms on the dolomite grains, to yield particles with Ca-sulphate rims and dolomite cores. These Ca-sulphate coatings on dolomite crystals are observed throughout the small columns (irrespective of height within the column) and suggests that once formed the Ca-sulphate rim creates a protective acid-resistant coating around the residual dolomite grain, inhibiting further Mg-leaching and dolomite dissolution. Furthermore it is known (Caceres, 2013) that magnesium preferentially leaches into solution, irrespective of the mineral host, over all other cations. This, coupled with the ready dissolution of carbonate minerals by strong acids, even if present only as a minor constituent of the fresh ore, will have a significant bearing upon the overall acid consumption figures within any ambient heap leach process as a whole.

The minerals identified in the fresh Çaldag ore and leached residues are summarised in Table 2.

### Table 2

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Fresh ore</th>
<th>Neutralisation (15days)</th>
<th>Primary leach (65days)</th>
<th>Complete leach (187 days)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Goethite</td>
<td>Goethite</td>
<td>Goethite</td>
<td>Goethite</td>
<td>Goethite</td>
</tr>
<tr>
<td>Quartz</td>
<td>Quartz</td>
<td>Quartz</td>
<td>Quartz</td>
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<tr>
<td>Dolomite</td>
<td>Dolomite</td>
<td>Dolomite</td>
<td>Dolomite</td>
<td>Dolomite</td>
</tr>
<tr>
<td>Kaolinite-smectite</td>
<td>Kaolinite-smectite</td>
<td>Kaolinite-smectite</td>
<td>Smectite</td>
<td>Smectite</td>
</tr>
<tr>
<td>Hematite</td>
<td>Hematite</td>
<td>Spinel</td>
<td>Spinel</td>
<td>Spinell</td>
</tr>
<tr>
<td>Fe-clinoclore</td>
<td>Spinel</td>
<td>Muscovite</td>
<td>Muscovite</td>
<td>Polygorskite</td>
</tr>
<tr>
<td>Muscovite</td>
<td>Lizardite</td>
<td>Magneteite</td>
<td>Muscovite</td>
<td>Muscovite</td>
</tr>
<tr>
<td>Lizardite</td>
<td>Talc</td>
<td>Anhydrite</td>
<td>Talc</td>
<td>Talc</td>
</tr>
<tr>
<td>Maghemite</td>
<td>Bassanite</td>
<td>Bassanite</td>
<td>Bassanite</td>
<td>Basanite</td>
</tr>
<tr>
<td>Calcite</td>
<td>Anhydrite</td>
<td>Amorphous matrix</td>
<td>Opal-CT</td>
<td>Maghemite</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Hematite</td>
<td>Basanite</td>
</tr>
</tbody>
</table>

Legend: italic = remain throughout; roman = mineral species identified that show no consistent trends; bold = disappears; bolditalic = forms. This summary infers that the Ca-sulphate species were precipitated as gypsum CaSO\textsubscript{4}-2H\textsubscript{2}O, however all these samples were dried at 110°C overnight prior to XRD analysis, a temperature sufficient to dehydrate gypsum to bassanite (CaSO\textsubscript{4}·1/2H\textsubscript{2}O) and/or anhydrite (CaSO\textsubscript{4}).

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**3.4. Leach solution behaviour**

Fig. 3 presents all the ICPAES underflow data collected between 0 and 127 days for the small column scale, with Fig. 4 showing the low concentration elements in more detail (expanded y-axes).

Of first note are the high Fe and S values as compared to all the other elements. Obviously the S level (presumably all as SO\textsubscript{4}\textsuperscript{2-} ions) reflects the fact that dilute H\textsubscript{2}SO\textsubscript{4} is used for leaching with the level gradually increasing to 160,000 mg l\textsuperscript{-1} as conc. H\textsubscript{2}SO\textsubscript{4} is added to maintain the desired 60 g l\textsuperscript{-1} free acid feed. Meanwhile, given that there was no Fe in the initial feed liquor, the 152,000 mg l\textsuperscript{-1} Fe concentration after 127 days must originate from the dissolution of the iron-rich goethite ore along with the degradation of acid-susceptible Fe-silicates. Throughout the leach cycle the amount of Fe in solution mirrors that of S (both in the underflow and feed). The suppressed Fe values between 10 and 30 days are due to a poor dilution procedure in use for these samples, this procedure was rectified for the post 30 day underflow solutions (see text). The vertical dashed lines indicate the end of neutralisation (15 days), primary leach (65 days) and secondary leach (127 days).

Examining the elements at lower concentrations shows a number of interesting trends. It appears that much of the Mg quickly leaches into solution, yet plateaus soon after at ~6500 mg l\textsuperscript{-1} Mg, perhaps reflecting that many of the Mg-containing minerals (particularly the layered silicates) present in the fresh ore are liable to collapse or disintegrate under the room temperature low pH experimental conditions. The roughly constant Mg concentrations in solution over time also indicate that no further dissolution or consumption/precipitation occurs, and therefore Mg is essentially a spectator ion in the leach cycle.

Al and Ni, however, have an initial concentration spike at ~8 days which then fades somewhat before generating a steadily
increasing concentration curve, ultimately achieving ~7000 mg l^{-1} Al and ~5500 mg l^{-1} Ni after 65 days and ~8500 mg l^{-1} Al and ~6700 mg l^{-1} Ni after 127 days. These Al and Ni plots reflect the fact that there is between 30–50% more Al than Ni in the fresh ore, Table 1, with the X-ray mapping studies showing that some is contained within the nickeliferous goethite, though the layered silicates and clay-like phases will also be Al hosts. The existence of differing slopes in the Al and Ni curves further suggest that these elements are leaching in different manners which in turn must reflect upon their (host) mineralogy and their coordination/residence states within these minerals, identification of which (by synchrotron methods, e.g. EXAFS, XPEEM; Carvalho-e-Silva et al., 2003; Singh et al., 2002) is beyond the scope of this work.

Mn and Cr, however, appear to leach at the same rate, though the Cr values are lower throughout. After 127 days ~1530 mg l^{-1} Mn and ~1280 mg l^{-1} Cr exist in solution, despite there being approx. 3 times more Cr in the fresh ore than Mn. This further confirms that Mn is more easily extracted at ambient temperature and therefore hosted in acid-susceptible phases. XRD shows that chromite, the spinel (Mg,Fe)(Cr,Al)O₄, is present, however it is well known that this mineral is particularly acid resistant and therefore would contribute to the difference between the fresh ore and observed Cr mg l^{-1} solution values. The underflow concentration curves for Co, K, P and Zn further mirror those of Mn and Cr, albeit at much reduced levels, such that after 127 days Co = 290 mg l^{-1}, K = 220 mg l^{-1} and P = Zn = 60 mg l^{-1} exist. Na concentrations, after an initial spike reaching 345 mg l^{-1} (6 days), are similar to those of P and Zn.

In contrast to the above Ca and Si exhibit exponentially negative extraction behaviours over time. Calcium has its highest concentration, Ca = 935 mg l^{-1}, in the first underflow solution with all subsequent analyses showing gradual loss of Ca in solution, down to a minimum of ~110 mg l^{-1} after 127 days. Realising that some of the Ca is contained within the calcite and dolomite phases in the fresh ore, and knowing that calcite will rapidly dissolve in strong acids whilst dolomite is more acid-resistant, being only slightly soluble in cold dilute mineral acids, easily explains why we find high Ca concentrations in the first leach liquors. The subsequent discovery of Ca-sulphate species in the column residues accounts for the decreasing Ca concentration in solution over time, as more and more Ca-sulphate precipitates, as gypsum CaSO₄·2H₂O, out of solution. Silicon similarly follows the calcium trend albeit at lower concentrations and has an initial spike of ~370 mg l^{-1} Si. Justification for such behaviour is more ambiguous given that the fresh ore contains ~11.6% Si with XRD showing that the main Si-containing mineral is quartz (which is particularly acid resistant), however all the clay-like phases are layered silicates and some will rapidly collapse upon contact with acid. It is possible, therefore that silicate structural collapse releases Si into solution (most likely to be as finely aggregated silica species, rather than Si ions) which then re(combines)precipitates over time to form colloidal or amorphous silica (5 mg l^{-1} Si at 127 days). Importantly, however, the presence of Si in solution implies that technically the Si-tie mass balance methodology should be applied with caution, since it assumes that Si is an immobile element in the system which is clearly not the case. Nevertheless the amount of Si leaching from the Çaldığ ore into solution, with respect to the bulk ore composition, is of the order of 0.004% of the total Si available, which at full scale could be considered negligible.

Examining trigonal plots for the small column underflows over the primary and secondary leach stages (15–127 days) shows that complex inter-relationships exist during leaching, Fig. 5. Considering the Ni–Fe–S plot, and given that the S and Fe levels in solution are 18–25 times more concentrated than Ni, their ratio response is almost linear and parallel to the S-axis. Thus as leaching occurs the initially clean H₂SO₄ acid solution becomes 'contaminated' with Fe and Ni, causing the data points to migrate from the initial (0Ni,0Fe,1S) apex towards the (0.03Ni,0.50Fe,0.47S) condition after 127 days leaching. In contrast the Co–K–Si plot, i.e. elements that are extracted in low concentrations, shows much more scatter, indicating a much weaker correlation exists. Thus at the end of neutralisation Si is the dominant component (0.13Co,0.22K,0.64Si), however this moves to a transition state (0.30Co,0.35K,0.35Si) after about 35 days leaching, with the ratio further shifting away from Si as the leaching time increases and Si precipitates out of solution. After 127 days the final condition is closer to (0.55Co,0.40K,0.05Si). Examining the Ni–Ca–Si diagram, where both Ca and Si precipitate out of solution as the leaching time progresses, shows that after neutralisation their inter-relationship steadily travels from (0.72Ni,0.18Ca,0.10Si) towards the 100% Ni condition (1Ni,0Ca,0Si) obtained after 127 days leaching. The Ca–Mn–Cr plot likewise reveals a constantly changing pattern. During leaching Ca precipitates whilst Mn and Cr form into a distinct relationship giving a well defined dataset with little scatter, which moves from (0.35Ca,0.45Mn,0.20Cr) at 15 days, through (0.20Ca,0.50Mn,0.30Cr) at 35 days to end with a (0.05Ca,0.55Mn,0.45Cr) ratio at 127 days. In contrast the data within the Ni–Mn–Cr diagram is essentially all focused upon the (0.75Ni,0.15Mn,0.10Cr) condition, thereby confirming that the extraction ratio for these three elements is pretty constant. The final tertiary plot shows that the Ni–Al–Mg inter-rela-

Fig. 5. Various element combination plots compiled using the post-neutralisation small column underflow data. Clockwise from top left: Ni–Fe–S, Co–K–Si, Ni–Ca–Si, Ni–Al–Mg, Ni–Mn–Cr, Ca–Mn–Cr; the arrows indicate the leaching time contribution to the datasets.
ship does alter, migrating from (0.2Ni,0.3Al,0.5Mg) at ~17 days to (0.3Ni,0.4Al,0.3Mg) by 127 days which signifies that after neutralisation both Ni and Al leach into solution at rates faster than Mg.

More constrained leach patterns emerge as the 4 m heap underflows are examined, Fig. 6. Here the datasets for Ca–Mn–Cr–Ni–Mn–Cr sit well within the scatter of their small column counterparts, however the values for the Ni–Al–Mg plot are aligned with their small column counterpart yet positioned towards the low Ni, low Al, high Mg apex between (0.11Ni,0.12Al,0.79Mg) and (0.18Ni,0.19Al,0.64Mg). This shift in the leach solution proportions indicates a relative increase in Mg in solution for the 4 m heap underflows as compared to the small column solutions and further suggests that Mg leaches preferentially into solution with Ni and Al dissolution being more time dependent. The reduced scatter in the 4 m heap datasets is a function of the leach scale, i.e. the intrinsic heterogeneity of the Ni-laterite ore becomes averaged such that it generates a truer representation of the bulk ore leach response.

3.5. Comparison of scale

Considering the leached solution element ratios in terms of their relationship to the corresponding fresh ore ratio gives an indication of the selectivity of the process. Thus a coefficient of selectivity, $K_s$, can be defined, Eq. (1), where $x$ and $y$ are the concentrations of the two elements under consideration, in mg l$^{-1}$ for the solutions and wt% for the ores. Extending this to examine the data as a function of time (0–127 days) and of experimental scale gives rise to Figs. 7 and 8, where the vertical dotted line at 15 days delineates the end of neutralisation and thus start of primary leach for the small column data.

$$K_s = \left(\frac{[x]/[y]}{[x]/[y]}\right)_{solution}$$

The selectivity of Ni over Fe in the leach liquors is indicative of the process efficiency and has an important bearing on the economics of the atmospheric heap leach model for any deposit. The Çaldag limonite exhibits good Fe/Ni selectivity during the initial days (neutralisation stage) of leaching across all scales. Bearing in mind the suppressed Fe values between 10 and 30 days for the small column solutions it is clear that after ~40 days differences emerge such that the small column underflows generally show no selectivity (Fe/Ni ~ 1) yet the 4 m heap solutions continue to leach Ni in preference to Fe (Fe/Ni ~ 0.5). This is as expected and confirms that an increase in the ore height for leaching yields better selectivity. The small column values show that more Fe is leached into solution and that there is insufficient height in the column for Fe re-precipitation. The mineral grain scale gives useful indicative information despite the scatter in the data, where the scatter is a function of the intrinsic heterogeneity of Ni-laterite ore and of the small 1 g mass of sampled grain fragments present initially. The bottle roll tests again give indicative selectivity values which reassuringly generally lie between the small column and 4 m heap data. As with the mineral grain scale the bottle roll values are heavily influenced by the composition of the fresh ore and its closeness, in terms of both mineralogy and chemistry, to the average bulk ore composition.

Interestingly after neutralisation no selectivity for the extraction of Mn versus Ni is shown (Mn/Ni ~ 1) and this is true at all the leach scales for which data is available (mineral grain 1 g fragments, small column and 4 m heap). It further confirms that Mn and Ni are extracted in constant proportions throughout.

The Mg/Ni and Mg/Al plots, meanwhile, demonstrate decreasing selectivity (exponential decay) with time such that initially more Mg, than Ni or Al, is in solution yet over time these ratios tend towards that of the bulk ore (Mg/Ni ~ 1.1 and Mg/Al ~ 1.4 in the small column underflows after 127 days). For both scenarios the leaching scale generates selectivity values which mirror data obtained across the different scales yet which show that extraction of Mg over that of Ni or Al from a 4 m heap is greatly enhanced over that from a small column. In contrast the mineral grain scale suggests that Ni leaches more easily than Mg (i.e. values constantly plot below the small column data, tending towards Mg/Ni = 0) however this is likely to be a reflection of the paucity of Mg-hosts in the goethitic fragments chosen at this scale. The 1 g mineral grain fragments gave Mg/Al selectivities slightly enhanced, though similar, to the small column data.

Chromium, in relation to manganese, does not readily leach into solution such that the observed selectivities range from Cr/Mn = 0.16–0.20 in the 4 m heap underflows to Cr/Mn = 0.16–0.28 in the small column underflows. These two leaching scales, therefore, give similar selectivities which reflect the predominant acid-resistant nature of their mineral hosts (e.g. Cr-spinel) such that following initial acid attack, upon Cr-rich layered silicates or goethite, only slow and gradual extraction of Cr into solution occurs over time.

The Ca plots (Ca/Ni, Ca/Mg and Ca/Mn) also exhibit low selectivities, as all plot with ratios of $K_s << 1$, however this is in line with Ca (as calcite or dolomite) being a minor constituent of the bulk ore, with Ni, Mg and Mn present in greater quantities and thus leaching

**Fig. 6.** Element combination plots compiled using post-neutralisation underflow data: (a) 4 m heap data only and (b) 4 m heap data and small column data superimposed. Left to right: Ca–Mn–Cr, Ni–Mn–Cr, Ni–Al–Mg plots; arrows indicate the leaching time contribution to the datasets.
more ubiquitously into solution. These selectivities show (exponentially) decreasing curves over time across all the leach scales examined and confirm that Ca leaches into solution (e.g. calcite dissolution) and thereafter precipitates out of solution (gypsum formation). Interestingly the mineral scale (1 g fragments) give Ca/Mn and Ca/Na selectivities more in keeping with the 4 m heap scale, presumably better reflecting the goethitic bulk mineralogy, than that obtained from the small column underflow data. The Ca/Mg selectivities are variable at the mineral grain scale (perhaps a reflection of the reduced Mg and Ca present in the fresh mineral-grain fragments) yet are consistently low for the 4 m heap (Ca/Mg < 0.14) and small column (Ca/Mg < 0.07) datasets, indicative of Mg leaching into solution in preference to Ca.

When cobalt is considered the selectivity plots across the different scales are revealing. Essentially the low concentration of Co present in the ore gives rise to unrealistic selectivity values at the mineral grain scale, being a reflection of the small amount (1 g) of material present, and illustrates the experimental limitations of this scale for inferring Fe/Co, Ni/Co or Mn/Co leach selectivities. Thus at the mineral scale the likelihood of fragments possessing very little, if any, cobalt, and thus being representative of the whole, is much greater than at other scales. Elsewhere the bottle roll, small column and 4 m heap selectivities compare favourably to each other. Throughout, the small column scale leaches more Fe, Ni and Mn into solution, as compared to Co (Fe/Co ~ 1.5, Ni/Co > 1.0 and Mn/Co > 1.0) whereas the 4 m heap underflows give consistent selectivities over time with Fe/Co ~ 0.80, Ni/Co ~ 1.25 and Mn/Co ~ 1.12. The bottle roll data shows more variation, with variable (often lower) selectivities in the initial stages of leaching which again may be a function of the reduced sample size (150 g) as compared to the small column (~8.6 kg) or 4 m heap scale (~4300 tonnes).

3.6. Applicability to other Ni-laterites

Clearly these results relate solely to the ambient dilute sulphuric acid leaching of nickeliferous limonite from the Çaldığ deposit in Turkey. Nevertheless a number of findings are widely applicable...
to other Ni-laterites, notably the rapid extraction of Mg$^{2+}$ into solution from all Mg-bearing mineral phases (Mg-silicates, dolomite etc.), the dissolution of calcite, formation of gypsum, developing porosity of nickeliferous goethite (over time) and the degradation of layered silicates, each with their corresponding impact upon the solution chemistry and residue integrity. In respect to full-scale heap leach metallurgical accounting and the impact upon leach behaviour (and by implication acid consumption) five key ‘driver elements’ can be identified: Mg, Fe, Al, Ni and Ca (Caceres, 2013; Marshall and Buarzaiga, 2004). Understanding the host mineralogy for these elements is critical in order to be able to establish how these elements will interplay and influence the leach behaviour at full scale.

4. Conclusions

This study has identified where true correlations exist between the different scales and where differences exist as a result of the testing at different scales. Given the intrinsic mineral heterogeneity of any Ni-laterite the role of sampling prior to experimental testing should not be underestimated and has a significant bearing upon the final leach results. Thus the mineral grain scale is inappropriate for determining Co selectivity and the small column scale gives limited Fe selectivity, as compared to bulk ore characteristics or the higher 4 m heap scale, respectively. Nevertheless Mn/Ni data across all scales is consistent and indicates that Mn and Ni are extracted from the Çaldag˘ Ni-laterite ore in constant proportions throughout. Equally the Ca–Mn–Cr and Ni–Mn–Cr inter-relationships are consistent across the small column and 4 m heap scales, with the larger heap data possessing reduced scatter, proportional to the increased mass of ore present.

A full and comprehensive mineralogical characterisation of any fresh Ni-laterite is a necessity, especially at the mineral grain scale, in order to understand the overall leach behaviour. Within the Çaldag˘ ore this is highlighted by the clear dissolution of calcite, CaCO$_3$ by the dilute sulphuric acid leach medium with subsequent precipitation as gypsum CaSO$_4$.2H$_2$O. Such data is hidden if only the bulk ore characteristics are considered, but will have a significant bearing upon the acid consumption rates during the leaching process.

Further academic study using synchrotron methods is required to ascertain the coordination chemistry of key elements within both the fresh ores and leached residues, and to hypothesise upon the associated mineral formation and leaching mechanisms (Carvalho-e-Silva et al., 2003; Singh et al., 2002; Fan and Gerson, 2011). In addition the amount of mobile Si in the system needs to be considered with respect to the Ni-laterite ore type (goethitic or siliceous) and the experiment scale (bottle roll or demonstration scale) when attempting Si-tie based mass balance calculations.

Finally it must be recognised that examining other correlations across these different scales (mineral grain scale to demonstration plant scale) is necessary before a true and complete predictive model can be developed. Such correlations would need to include acid consumption, elemental extraction, leaching cycle stage (neutralisation, primary leach, secondary leach, washing etc.), leaching cycle duration, amongst others.
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