

Article

# Iron Control in Atmospheric Acid Laterite Leaching

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**Abstract:** Iron control in the atmospheric acid leaching (AL) of nickel laterite was evaluated in this study. The aim was to decrease acid consumption and iron dissolution by iron precipitation during nickel leaching. The combined acid leaching and iron precipitation process involves direct acid leaching of the limonite type of laterite followed by a simultaneous iron precipitation and nickel leaching step. Iron precipitation as jarosite is carried out by using nickel containing silicate laterite for neutralization. Acid is generated in the jarosite precipitation reaction, and it dissolves nickel and other metals like magnesium from the silicate laterite. Leaching tests were carried out using three laterite samples from the Agios Ioannis, Evia Island, and Kastoria mines in Greece. Relatively low acid consumption was achieved during the combined precipitation and acid leaching tests. The acid consumption was approximately 0.4 kg acid per kg laterite, whereas the acid consumption in direct acid leaching of the same laterite samples was approximately 0.6–0.8 kg acid per kg laterite. Iron dissolution was only 1.5–3% during the combined precipitation and acid leaching tests, whereas in direct acid leaching it was 15–30% with the Agios Ioannis and Evia Island samples and 80% with the Kastoria sample.

**Keywords:** laterite; nickel; leaching; jarosite; precipitation

## 1. Introduction

Nickel is an essential element for modern industry with uses in stainless steel, nickel-based alloys, casting and alloy steels, electroplating, and rechargeable batteries [1,2]. The global plant production and demand for nickel in 2015 were 1.93 Mt and 1.88 Mt, respectively [3]. Nickel mine production has increased steadily during the past 50 years; however, from 2008 onwards it has been more rapid. A further increase in demand may be encountered due to the higher production numbers of electric vehicles (EVs) as nickel is an essential battery chemical in typical lithium ion batteries [4]. The global reserves of nickel are estimated to be 74–80 Mt including sulphide ores, laterites, and deep-sea nodules [4,5]. Even though laterites represent the vast majority of land-based reserves (approximately 72%), until 2009, less than half of the global nickel production came from nickel laterite ores. Today, more than 60% of the world's nickel is derived from laterite resources [6–9]. To meet the rising nickel demand in the future, it is essential to develop further the methods that allow the economic utilization of nickel laterite ores.

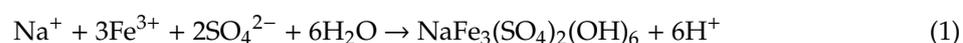
Laterite deposits often contain several laterite types. Limonite laterites are found near the surface, while saprolite ores exist deeper and underneath the limonite ores [10]. The iron content of limonites is usually high and a significant amount of nickel is associated with it, whereas the iron content of saprolites is lower and the nickel is more often associated with silicates. Nickel is also found to be more readily leached from clay-like saprolite ores than limonites [6]. It is typical that Greek laterites contain some of the iron as hematite rather than goethite, which allows the leaching of nickel under conditions mild enough to avoid the high acid consumption associated with the substantial dissolution of iron [6].

At the moment, high-pressure acid leaching (HPAL) and pyrometallurgical treatment are the two main technologies for nickel laterite processing [11,12]. However, they have some disadvantages, such as high autoclave investment costs [6,13], technical problems [14], and high energy consumption [11]. In addition, these processes require rather high-grade nickel laterite ore for feasible operation. Ashok [11] has stated that the nickel content of ore should be over 1.4% for feasible HPAL processing and over 1.7% for pyrometallurgical processing.

The third option for nickel laterite processing is atmospheric acid leaching (AL). Investment costs of the process are lower than for pressure leaching, while the need for energy is significantly lower than for the pyrometallurgical operation [6]. Another advantage of AL is the potential to valorize the leach residues. Komnitsas et al. [15] found that column leaching residues can be alkali activated with the use of NaOH and Na<sub>2</sub>SiO<sub>3</sub> as activators. Inorganic polymers with high strength, almost 40 MPa, can be produced, when 10 wt % metakaolin is added to the residue. These low toxicity products can be used as binders or building materials in several applications in the construction sector.

The main disadvantages of the AL process are high acid and neutralization agent consumptions. Usually, a significant fraction of total nickel content of laterite ore is associated with iron. Nickel may substitute iron in iron oxide minerals like goethite and thus selective leaching of nickel is not possible, as the chemical decomposition of the goethite is needed for nickel dissolution [10,11]. In the HPAL process, most of the dissolved iron will eventually precipitate as hematite, but in the case of the AL process, it will end up in the solution and must be removed before nickel recovery [16]. During laterite leaching, iron removal from the pregnant solution is usually carried out by using limestone [17] and, depending on the iron concentration, this can be a significant cost item. Therefore, effective iron control is necessary in order to minimize acid consumption and neutralization costs in atmospheric acid laterite leaching.

The main objective of this study was to combine nickel leaching and iron precipitation as sodium jarosite. The idea of combined leaching of limonite and using saprolite for neutralization has been patented by Arroy and Neudorf [18]. In this patent, limonite is dissolved with mineral acid and the saprolite type of laterite is used as neutralizing agent for jarosite precipitation. This invention decreases the use of additional neutralization agent for iron removal and thus improves the feasibility of the process. A quite similar idea, mostly for the sulfide type of nickel ores, has been patented by Leppinen et al. [19]. The patent's idea is to use poor nickel ore or waste for pH adjustment after the atmospheric acid leaching of nickel, cobalt, copper, or zinc. Iron dissolved in the atmospheric leaching precipitates and acid generated during the iron precipitation reaction is used for nickel dissolution from poor nickel ore. Jarosite precipitation is widely applied in hydrometallurgy to remove iron from the pregnant leach solution (PLS). In 2013, White and Gillaspie [20] reviewed comprehensively the acid leaching of nickel laterites with jarosite precipitation, including a discussion on the laterite profile as well as the disposition of other elements. In sulfuric acid solutions, sodium jarosite (NaFe<sub>3</sub>(SO<sub>4</sub>)<sub>2</sub>(OH)<sub>6</sub>) forms in the presence of dissolved ferric (Fe<sup>3+</sup>) and sodium (Na<sup>+</sup>) ions according to the following reaction:



Reaction (1) produces acid and has a positive effect on the acid consumption of the process. Favorable conditions for the reaction are pH < 2.5 and temperature 80–100 °C [21,22].

This study's specific aim was to investigate simultaneous nickel leaching and jarosite precipitation using Greek laterites. Investigating the characteristics of laterite ores and their suitability for simultaneous leaching and iron precipitation is the first step for the development of a feasible process. If iron control is successful in batch tests, pilot tests will be designed based on these results in the next phase of the research.

## 2. Materials and Methods

### 2.1. Materials

Three nickel laterite ore samples were obtained from the GMM LARCO SA mines. The origin of the ores are the mines of Agios Ioannis (LAI) and Evia Island (LEV), in central Greece, and Kastoria (LK) in northwestern Greece. The comminution of the samples to  $-300\ \mu\text{m}$  was carried out by Technical University of Crete, Chania, Greece. Each sample (i.e., LAI, LEV, and LK) was divided into sub-samples at VTT by using a sample divider (FRITSCH Rotary Sample Divider LABORETTE 27 and FRITSCH Vibratory Feeder LABORETTE 24, Pittsboro, NC, USA). The dry matter content (% DM) of the samples was determined at VTT from the mass difference after drying the samples at  $105\ ^\circ\text{C}$ . Dry matter contents were LAI 98.6% DM, LEV 99.2% DM, and LK 98.0% DM.

The chemical and mineralogical composition of the samples was studied at Outotec, Espoo, Finland. The composition of the samples was analyzed by inductively coupled plasma optical emission spectrometry (ICP-OES) after total dissolution. Sulfur and carbon analysis was measured using an Eltra CS-2000 automatic analyzer. The quantity of silica was analyzed colorimetrically using a Hach DR 5000 UV-Vis spectrophotometer. The chemical compositions of the laterite samples are presented in Table 1. X-ray diffraction (XRD) analysis for the ores was carried out at Outotec, Espoo, Finland and the analysis for the leach residues was performed at Eurofins Expert Services Oy, Espoo, Finland.

In addition to XRD analysis used to determine the main minerals of each ore sample, polished sections were prepared from each sample, and they were examined by a JEOL JSM-7000F field emission scanning electron microscope (FE-SEM) (Tokyo, Japan) equipped with an Oxford Instruments energy dispersive spectrometer (EDS) and wavelength dispersive spectrometer (WDS). The imaging and both EDS and WDS analyses were performed under routine conditions using 20 kV acceleration voltage and 1 nA beam current for EDS analyses and 20 nA beam current for WDS analyses. The minerals were identified from the EDS analyses and their nickel content was analyzed by WDS using a pure nickel metal standard. Mineral quantification was performed using HSC Chemistry<sup>®</sup> (Module version 9.3.0, Outotec, Espoo, Finland) using mineralogical analyses gathered from all of the aforementioned methods. The mineralogy of the laterite samples and the distribution of nickel within the minerals are presented in Table 2.

**Table 1.** Chemical composition of the laterite samples.

Laterite	LAI	LEV	LK
Element	%	%	%
Ni *	1.00	0.843	0.939
Fe *	31.6	26.3	13.2
Al *	9.58	2.62	0.388
Mg *	1.1	2.16	12.8
Na *	<0.1	<0.1	<0.1
P *	0.025	<0.02	<0.02
K *	0.16	0.539	<0.1
Ca *	2.2	2.08	3.37
Ti *	0.55	0.142	0.025
Cr *	1.27	1.72	0.554
Mn *	0.179	0.167	0.179
Co *	0.062	0.042	0.029
Cu *	<0.005	<0.01	<0.01
Zn *	0.015	0.015	0.009
As *	0.02	<0.02	<0.02
C **	0.69	0.76	1.1
S **	0.02	0.09	<0.02
SiO <sub>2</sub> ***	16.3	40.7	37.1

Sample methods: \* ICP TOT, \*\* Eltra, \*\*\* Colorimetry.

**Table 2.** Mineralogy of the samples and distribution of nickel in each main phase.

Mineralogy	LAI	Ni	LEV	Ni	LK	Ni
	wt %	dist. %	wt %	dist. %	wt %	dist. %
Hematite	45.4	16	44.6	47		
Goethite					19.5	24
Al-clays and Al-hydroxides *	21.1	60				
Smectite group minerals	5.5	22	2.1	13		
Primary serpentinite silicates **	12.8	1	8.5	39	67.6	75
Quartz	6		34.4		3.2	
Carbonates	5.8		3.3		7.6	
Chromite	2.6	<1	3.5	<1	1.7	<1
Magnetite	0.8	<1	0.7	<1	0.5	<1

\* The content of aluminum clays and aluminum (oxy)hydroxides cannot be assessed with the characterization methods used; \*\* LAI, chlorite and anthophyllite; LEV, chlorite; LK, lizardite and anthophyllite.

Based on mineralogical analyses, LAI is composed mainly of hematite, clays, and primary serpentinite silicates. Nickel is distributed into mainly (60%) Al-clays and Al-hydroxides and the rest is distributed into smectites and hematite. Based on the mineralogical analyses of the samples, LAI was found to be a mixture of different laterization profiles. It could be defined as an aluminous laterite or a bauxite, based on its high Al content. However, the occurrence of smectites, primary serpentinite silicates, and the high contents of Fe and hematite are typical features of saprolitic and limonitic laterization profiles as well as weathered serpentinite.

LEV is composed mainly of hematite and quartz. Minor chlorite, smectite, chromite, and carbonates comprise the rest of the sample. With respect to the nickel, 47% of it is distributed into hematite, 39% into chlorite, and 13% into the smectites. Based on the mineralogy, LEV was mined from a transitional zone, between limonitic and saprolitic profiles.

In the case of LK, 68% of it is composed of primary serpentinite silicates (i.e., lizardite and anthophyllite), 20% of goethite, 7.6% of calcite and dolomite, 3.2% of quartz, and 1.7% of chromite. LK can be categorized as weathered serpentinite laterite. Its nickel is mainly (75%) distributed into the primary serpentinite silicates and secondarily (24%) into goethite.

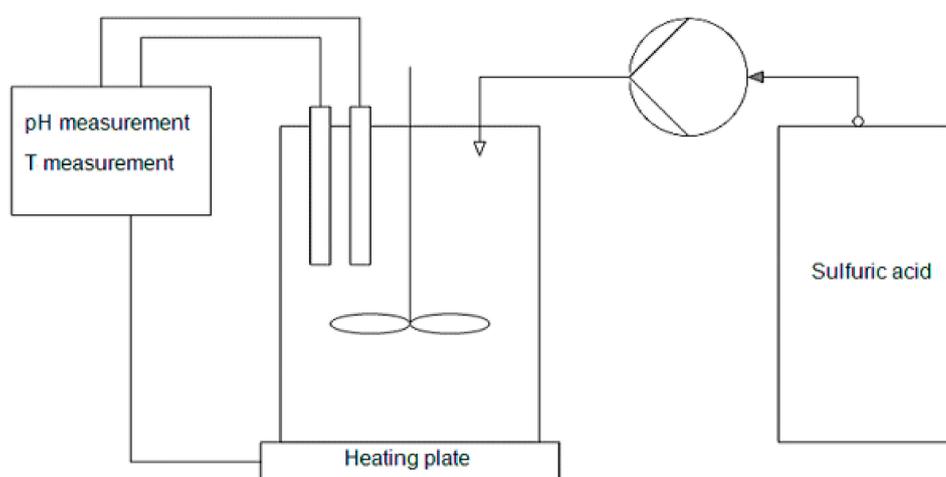
Theoretical maximum acid consumptions of the laterite samples are presented in Table 3. The acid consumption is calculated for each metal assuming that the metal dissolution is 100%. It can be seen from the table that acid-consuming metals are quite different in each sample. The main acid-consuming metals in the LAI sample are iron and aluminum, while the aluminum content of the LEV sample is very low and iron is the only significant acid-consuming metal. Acid consumption in both LEV and LAI samples is mainly caused by iron, but in case of the LK sample, the main acid-consuming metal is magnesium.

**Table 3.** Theoretical maximum acid consumption of Agios Ioannis (LAI), Evia Island (LEV) and Kastoria (LK) laterites as grams sulfuric acid per kg laterite. Metal dissolution to solution is assumed to be 100%.

	LAI	LEV	LK
	H <sub>2</sub> SO <sub>4</sub> g/laterite kg	H <sub>2</sub> SO <sub>4</sub> g/laterite kg	H <sub>2</sub> SO <sub>4</sub> g/laterite kg
Ni	16.7	14.0	15.7
Fe	832	693	348
Al	522	143	21.3
Mg	44.4	87.2	517
Ca	53.8	50.9	82.5
Mn	3.21	3.03	3.21
Total	1470	991	987

## 2.2. Leaching of Laterite Ores

The aim of the study was to determine whether a suitable feed consisting of LAI, LEV, and LK ores would result in iron control during atmospheric acid leaching. In the first phase of the tests, the effect of pH on nickel and iron dissolution was determined. The leaching test setup is presented in Figure 1. In the experiments, a Mettler Toledo T70 titrator (Columbus, OH, USA) was used for H<sub>2</sub>SO<sub>4</sub> feed and a Consort C3040 was used to monitor pH, oxidation/reduction potential (ORP), and temperature on-line. Manufacturer and model of the electrodes were Van London Phoenix PH7V110-10B-300 (pH electrodes) and Van London Phoenix RP75130-10B-300 (oxidation/reduction electrodes) (Houston, TX, USA). The reactor mass was monitored by a balance, Shimadzu BW22KH (Kyoto, Japan) or Hottinger Baldwin Messtechnik GmbH (Darmstadt, Germany), connected to a monitor, Gottl. Kern & Sohn GmbH (Balingen, Germany). In the experiments where LK was added, the amount of LK addition was examined on-line by a balance, Precisa ES 8200C-DR (Aldingen, Germany). Chemicals used in the experiments were H<sub>2</sub>SO<sub>4</sub> (Merck EMSURE® ISO sulfuric acid 95–97% for analysis) and Na<sub>2</sub>SO<sub>4</sub> (Sigma-Aldrich sodium sulfate ACS reagent ≥99.0% anhydrous granular, St. Louis, MO, USA).



**Figure 1.** Experimental setup used in the acid consumption test. A 5 L reactor (Ti, Gr. 2) on the heating plate is placed on top of the balance. Titrator is on the right.

The characteristic leaching behavior of each laterite was studied under the following leaching conditions: pH 0.25–1.5, T = 90 °C, S/L = 30%, particle size –300 µm, 800 rpm. Experiments were carried out in 5 L reactors for 8 h. An experiment started (t = 0 h) when the target pH was reached.

Based on the results of the 8 h leaching tests, two-phase leaching tests were designed. These experiments were carried out in pH 0.75–1.8, T = 90 °C, S/L = 30%, particle size –300 µm, 800 rpm, 48 h. In the first part of these tests, LAI or LEV were first leached separately at pH 0.75. LAI was leached for 24 h and LEV for 6 h. In the second part of the tests, leaching was continued for the following 24 h in pH 1.8 with LK addition. In the tests, pH was controlled by LK additions and H<sub>2</sub>SO<sub>4</sub>. Iron precipitation was ensured by Na<sub>2</sub>SO<sub>4</sub> additions before the LK feed. The amounts were 235 g of Na<sub>2</sub>SO<sub>4</sub> for LAI and 150 g for LEV.

After leaching, the slurry was filtered (pore size of 0.45 µm) using a Büchner funnel and a filter flask. The leach residue was washed with acidic water (pH 1–1.5), followed by a washing with deionized water. The washed residue was dried and weighed.

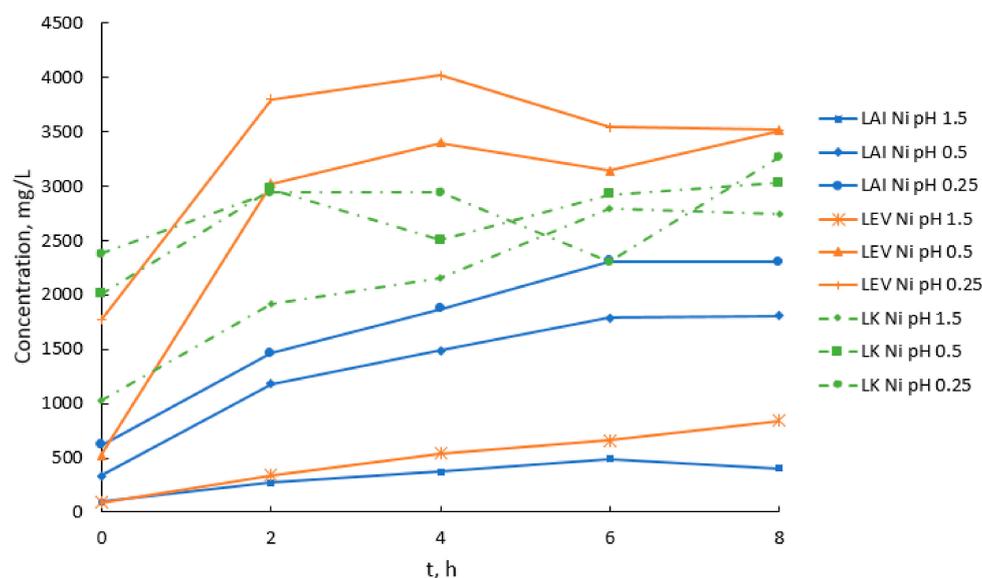
## 2.3. Analytical Methods

Solution samples were analyzed with ICP-OES and ICP-MS. Microwave-assisted digestion was performed with a mixture of HF, HNO<sub>3</sub>, and HCl according to EN 13656 and the subsequent determination of elements was applied to solid samples. These analyses were carried out at Labtium Oy, Espoo, Finland.

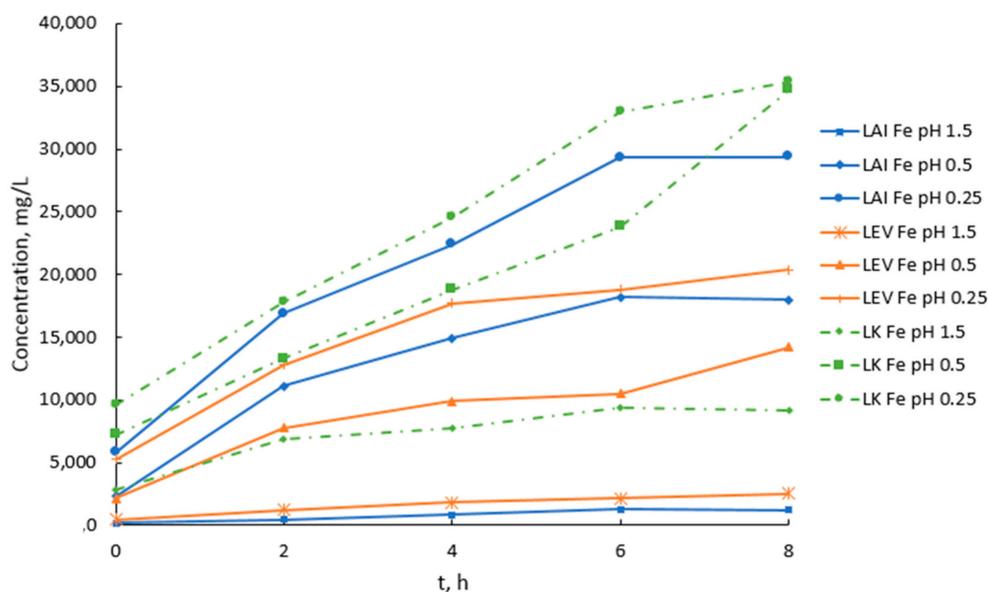
### 3. Results and Discussion

#### 3.1. Acid Leaching of Greek Laterites

Sulfuric acid leaching tests were carried out for each LAI, LEV and LK laterite sample. The idea of the leaching tests was to find suitable leaching pH for each laterite and determine acid consumption of direct acid leaching. Nickel dissolution during the 8 h leaching tests is presented in Figure 2 and iron dissolution in Figure 3. The nickel and iron recoveries are shown in Table 4.



**Figure 2.** Evolution of Ni concentration vs. time during leaching of LAI, LEV, and LK laterites in pH 0.25, 0.5, and 1.5. Parameters used in the experiments: 90 °C, S/L = 30%, 800 rpm. pH was maintained by H<sub>2</sub>SO<sub>4</sub> addition.



**Figure 3.** Evolution of Fe concentration vs. time during leaching of LAI, LEV, and LK laterites in pH 0.25, 0.5 and 1.5. Parameters used in the experiments: 90 °C, S/L = 30%, 800 rpm. pH was maintained by H<sub>2</sub>SO<sub>4</sub> addition.

**Table 4.** Nickel and iron yields to solution in acid leaching test of LAI, LEV, and LK laterite in pH 0.25, 0.5 and 1.5. Parameters used in the experiments: 90 °C, S/L = 30%, 800 rpm. pH was maintained by H<sub>2</sub>SO<sub>4</sub> addition.

	LAI, pH 1.5	LAI, pH 0.5	LAI, pH 0.25	LEV, pH 1.5	LEV, pH 0.5	LEV, pH 0.25	LK, pH 1.5	LK, pH 0.5	LK, pH 0.25
Ni, %	12.0	54.3	69.0	30.1	>100.0	>100.0	87.5	96.8	>100.0
Fe, %	1.2	17.1	27.9	2.9	16.2	23.3	20.9	78.9	80.5

The mineralogical study shows that a significant portion of nickel in LAI and LEV laterites is associated with iron oxides and iron-containing silicates and it seems, based on the leaching results, that a partial decomposition of these minerals is needed for nickel liberation and dissolution. Nickel dissolution kinetics in LEV leaching tests was fast and maximum nickel dissolution was achieved only four hours from the beginning of the test. Iron dissolution was relatively low in the LEV leaching tests. Based on these results, it can be concluded that, in LEV laterite, nickel is not substituted into goethite like in many limonite laterites [6,7]. In the LAI leaching tests, the nickel was harder to leach and was associated with more refractory host minerals. Nickel dissolution from LK laterite was found to differ compared to nickel dissolution from LAI and LEV samples. Most of the nickel was dissolved already at pH 1.5. Most of the LK (67.6 wt %) consists of primary serpentinite silicates, such as lizardite (Mg<sub>3</sub>Si<sub>2</sub>O<sub>5</sub>(OH)<sub>4</sub>) and anthophyllite (Mg<sub>7</sub>(Si<sub>8</sub>O<sub>22</sub>)(OH)<sub>2</sub>), and 75% of the nickel is associated with these silicates. Only 19.5 wt % of LK consists of hematite and other iron oxides, and 24% of the nickel is associated with these oxides. Therefore, it is clear that iron dissolution is not associated with nickel dissolution.

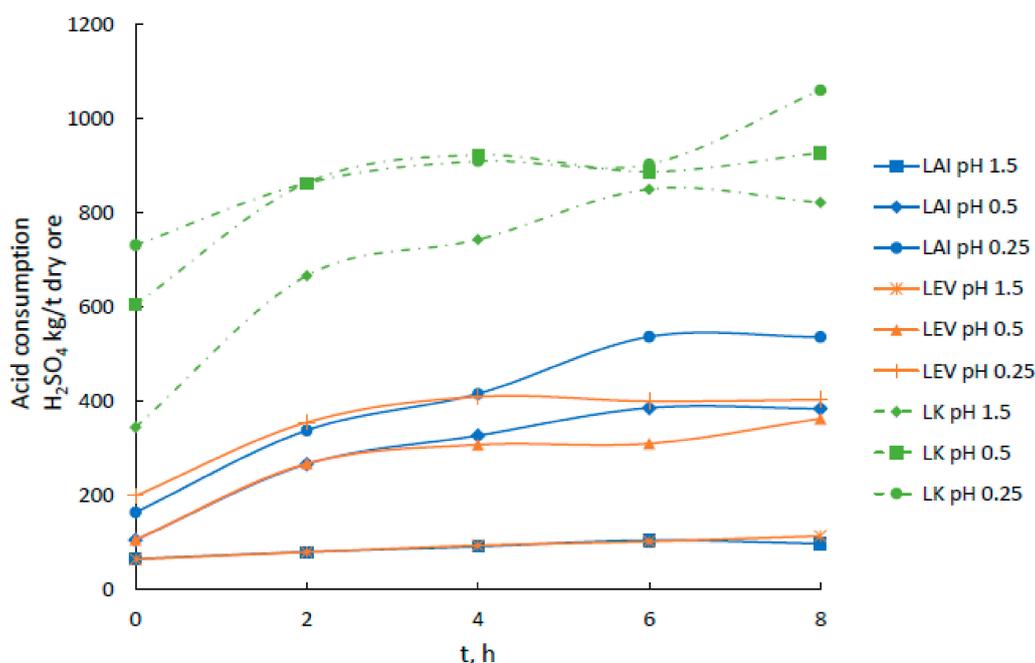
It can be seen from Figures 2 and 3 that nickel dissolution of LAI and LEV laterites at pH 1.5 is much lower than at pH 0.5 and 0.25. Higher acidity was needed for efficient nickel dissolution for LAI and LEV laterites. In contrast, nickel from LK dissolved considerably already at pH 1.5 and the dissolution was quite similar in all LK leaching tests. Some oscillation in the nickel concentrations was observed; this is most likely related to the addition of acid followed by the subsequent dissolution of metal. Nickel yields at pH 1.5 were 12% for LAI, 30.1% for LEV, and 87.5% for LK (see Table 4). However, the iron dissolution of LK was significantly higher when the pH was 0.25–0.5 compared to the test carried out at 1.5.

When comparing the nickel and iron dissolution at pH 0.5 and 0.25 (see Figures 2 and 3), it is observed that nickel cannot be selectively dissolved because a significant fraction of iron will also dissolve together with the nickel. Theoretical acid consumptions for the laterite samples are presented in Table 3 and actual acid additions after 8 h of leaching are presented in Table 5. The actual amounts of acid consumed in the leaching reactions are presented in Figure 4. Acid addition was calculated based on the amount of sulfuric acid (100%) added to the leaching reactor divided by the amount of dry laterite added to the reactor. Acid consumption was calculated from the metal dissolution rate, assuming that Mg, Mn, and Ni consume 1 mol acid per 1 mol metal and that Fe and Al consume 1.5 mol acid per 1 mol metal. It was found out that acid addition in both LAI and LEV tests was quite low, being only approximately 120–140 kg sulfuric acid per t laterite when the pH was 1.5. Acid additions and calculated acid consumption values are quite similar, indicating that the amount of unreacted acid is very low. Acid addition in the LK leaching test was significantly higher than in LAI and LEV leaching at the same pH, being 650 kg sulfuric acid per t laterite. The metal concentrations in the final leach solutions are shown in Table 6. It can be concluded that the high acid addition of LK laterite at pH 1.5 is mainly due to high magnesium dissolution. Based on the acid consumption calculation, nearly 80% of the acid was consumed in the magnesium dissolution reactions. It seems that dissolution kinetics of magnesium from silicates is relatively fast since most of acid was consumed during the two hours from the beginning of the test. Acid addition in the LK leaching tests was close to the theoretical maximum acid consumption when pH was 0.5 or 0.25. Acid addition in the LAI and LEV leaching tests was low compared to the theoretical maximum consumption. This is mainly

explained by the relatively low iron dissolutions. Iron, however, was still the main acid-consuming metal in both the LAI and LEV leaching tests. Approximately 30% of the total acid consumption was caused by iron dissolution in the LEV leaching test and approximately 40% in the LAI leaching test. There are significant differences between acid addition and calculated acid consumption values at pH 0.5 and 0.25. There was some oscillation in the acid addition and calculated acid consumption values, but it seems that the amount of unreacted acid at pH 0.5 is approximately 50 kg per t ore, whereas at pH 0.5 it is somewhat higher at over 100 kg per t ore.

**Table 5.** Cumulative acid additions ( $H_2SO_4$  kg/t dry ore) during leaching of the LAI, LEV, and LK laterites in pH 0.25, 0.5, and 1.5. Parameters used in the experiments: 90 °C, S/L = 30%, 800 rpm. pH was maintained by  $H_2SO_4$  addition.

pH	Time	LAI	LEV	LK
	h	$H_2SO_4$ kg/t dry ore	$H_2SO_4$ kg/t dry ore	$H_2SO_4$ kg/t dry ore
1.5	2	72.9	89.3	532
	4	92.5	115	597
	6	109	126	647
	8	123	142	647
0.5	2	305	343	787
	4	372	403	832
	6	395	455	1120
	8	442	455	1120
0.25	2	463	4940	880
	4	532	529	911
	6	605	576	945
	8	649	593	951



**Figure 4.** Calculated acid consumptions ( $H_2SO_4$  kg/t dry ore) during leaching of the LAI, LEV, and LK laterites in pH 0.25, 0.5, and 1.5. Parameters used in the experiments: 90 °C, S/L = 30%, 800 rpm. pH was maintained by  $H_2SO_4$  addition. Acid consumptions were calculated based on solution analyses.

**Table 6.** Dissolutions of Ni, Co, Fe, Ca, Mg, and Al and efficiency of H<sub>2</sub>SO<sub>4</sub> leaching of the LAI, LEV, and LK laterites under the following conditions: pH 0.25, 0.5, and 0.25, 90 °C, S/L = 30%, 8 h. Selectivity of Ni is compared over Fe, Mg, and Al using the respective ratios and concentrations in the pregnant leach solution (PLS).

Laterite Ore	pH	Ni (mg/L)	Co (mg/L)	Fe (mg/L)	Ca (mg/L)	Mg (mg/L)	Al (mg/L)	Ni/Fe	Ni/Mg	Ni/Al
LAI	1.5	401	60	1220	447	591	1560	0.33	0.68	0.26
LAI	0.5	1810	156	18,000	515	2630	9020	0.10	0.69	0.20
LAI	0.25	2300	174	29,400	405	2990	12,400	0.08	0.77	0.19
LEV	1.5	845	27	2550	721	2350	1440	0.33	0.36	0.59
LEV <sup>1</sup>	0.5	3510	136	14,200	518	8040	5210	0.25	0.44	0.67
LEV	0.25	3520	77	20,400	417	7540	5070	0.17	0.47	0.69
LK	1.5	2740	63	9210	373	53,400	437	0.30	0.05	6.27
LK	0.5	3030	60	34,700	159	44,900	754	0.09	0.07	4.02
LK	0.25	3270	85	35,400	177	55,300	785	0.09	0.06	4.17

<sup>1</sup> Sample treatment from t = 8 h was unsuccessful. Analysis was done after 26.5 h. In this experiment, 8 h of leaching was performed at 90 °C, and then the slurry was agitated without heating overnight.

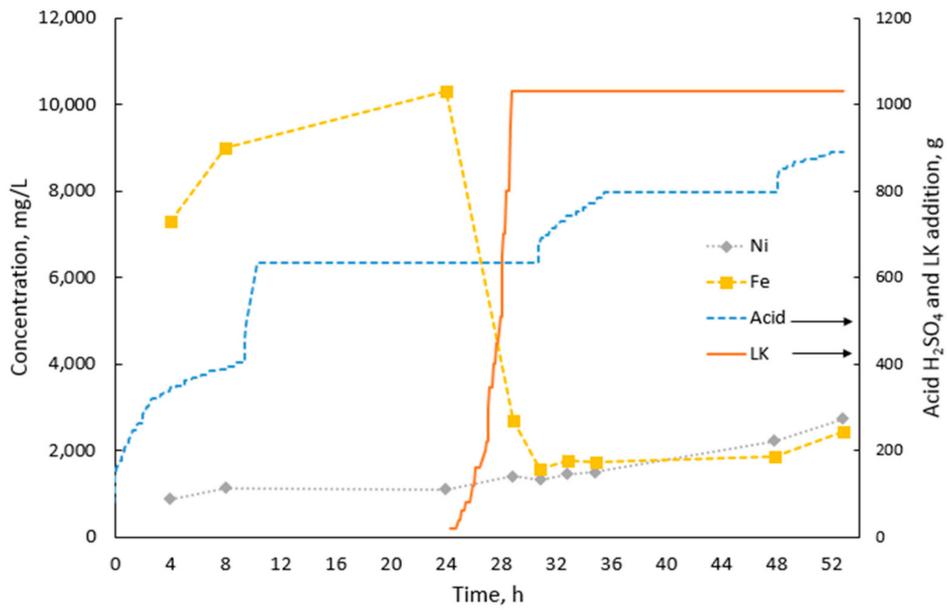
The 8 h leaching experiments showed that nickel from LK laterite can be dissolved at pH 1.5, which is also a suitable pH for jarosite precipitation. It was found that LAI and LEV need more acidic conditions, while simultaneous nickel leaching and jarosite precipitation in these cases is not possible. The combined leaching and precipitation tests were designed based on these facts.

### 3.2. Combined Leaching and Iron Precipitation

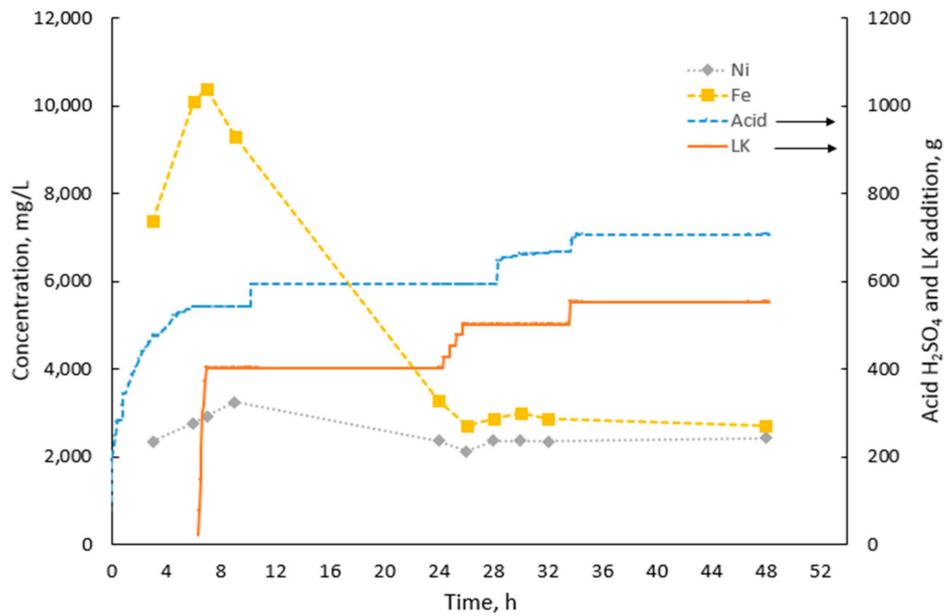
The aim of the combined leaching and iron precipitation tests was to dissolve nickel from LEV or LAI laterite first in a lower pH and then to increase the pH by LK addition. This would allow for the simultaneous dissolution of nickel from LK and precipitation of iron from the solution.

Combined tests began by leaching LAI or LEV laterites at pH 0.75, followed by an increase of pH to 1.8 by LK laterite addition. Leaching was continued until a total leaching time of 48 h was reached. The duration of the first leaching phase was decided for LAI and LEV based on the results of the 8 h experiments. As metallurgical process design involves balancing costs and yields, the question of whether leaching at pH 0.75 would be sufficient for nickel dissolution from LAI and LEV was studied. In Figure 2, it was seen that at pH 0.5 and 0.25, a significant dissolution of nickel from LEV occurred already after 2 h leaching. Therefore, the leaching time for LEV was determined to be 6 h. Based on the 8 h test, nickel dissolution from LAI was slower than from LEV. As seen from Table 4, the nickel yield from LAI after 8 h increased from 54.3% to 69.0% when pH was decreased from 0.5 to 0.25. Thus, the leaching time selected for LAI at pH 0.75 was 24 h.

Ni, Co, Fe, Ca, Mg, and Al dissolution, acid addition, and LK consumption during the combined leaching, and the iron precipitation experiments are shown in Figures 5 and 6 as well as in Table 7. A clear decrease in iron concentration is noticed after LK addition. In both cases, iron concentration after leaching of LAI or LEV was over 10 g/L, and after the LK addition the iron concentration decreased to approximately 2 g/L. Table 7 shows the efficiency of H<sub>2</sub>SO<sub>4</sub> leaching of laterites in combined nickel leaching and iron precipitation tests, by comparing the selectivity of Ni over Fe, Mg, and Al using the respective ratios and concentrations in the PLS. As can be seen in Figures 5 and 6, iron precipitation was clearly observed after LK addition. In Table 7, this is shown also by the high Ni/Fe selectivity values.



**Figure 5.** Leaching of LAI for 24 h at pH 0.75, followed by LK laterite addition increasing the pH to 1.8. Concentrations of Ni, Co, Fe, acid, and LK additions. Parameters used in the experiments: 90 °C, S/L = 30%, 800 rpm.



**Figure 6.** Leaching of LEV for 6 h at pH 0.75, followed by LK laterite addition increasing the pH to 1.8. Concentrations of Ni, Co, Fe, acid, and LK additions. Parameters used in the experiments: 90 °C, S/L = 30%, 800 rpm.

**Table 7.** Efficiency of H<sub>2</sub>SO<sub>4</sub> leaching of LAI (24 h) and LEV (6 h) laterites under the following conditions: pH 0.75, 90 °C, S/L = 30%, followed by LK addition to increase pH to 1.8 (until 48 h), by comparing the selectivity of Ni over Fe, Mg, and Al using the respective ratios and concentrations in the PLS.

Laterite Ore	pH	Ni (mg/L)	Co (mg/L)	Fe (mg/L)	Ca (mg/L)	Mg (mg/L)	Al (mg/L)	Ni/Fe	Ni/Mg	Ni/Al
LAI	0.75	1100	82	10300	595	1630	6040	0.11	0.68	0.18
LAI + LK	1.8	2220	124	1850	456	24100	2000	1.2	0.09	1.11
LEV	0.75	2770	119	10100	-	6510	4560	0.27	0.43	0.61
LEV + LK	1.8	2430	94	2710	-	19300	2520	0.90	0.13	0.96

The Ni/Fe ratio that defines selectivity, when LAI was separately leached at pH 0.75, was 0.11. Komnitsas et al. [13] also studied leaching of ore from a similar origin. Their column leaching test for a lower grade Agios Ioannis ore (0.58% Ni) resulted in Ni/Fe ratios varying between 0.15 and 0.24. Mystrioti et al. [23] applied a counter-current mode of operation for HCl leaching of a similar ore which suppressed iron dissolution to 0.6%. However, they found out that the operation had a negative effect on Ni and Co extraction, which was limited to 55% and 63%, respectively. At the moment, the sulfuric acid leaching approach applied in this study appears to be more favorable in terms of Ni leaching.

Nickel concentration after leaching at pH 0.75 was 1100 mg/L for LAI and 2770 mg/L for LEV. This is in line with the dissolution results after 8 h leaching. Ni concentrations for LAI were 401 mg/L at pH 1.5 and 1810 mg/L at pH 0.5. Ni concentrations for LEV were 845 mg/L at pH 1.5 and 3510 mg/L at pH 0.5. After 48 h leaching, Ni concentrations were 2220 mg/L for LAI + LK and 2430 mg/L for LEV + LK.

Acid additions of the combined tests are presented in Table 8. Acid additions were 370 kg sulfuric acid per 1 t ore for the LAI + LK test and 420 kg sulfuric acid per 1 t ore for the LAI + LK test, whereas in direct acid leaching acid additions were approximately 500–900 kg sulfuric acid per 1 t laterite ore. Acid consumptions calculated using solution analyses were quite close to the actual acid consumptions. The calculated acid consumption in the LAI + LK test was 415 kg sulfuric acid per t ore, and in the LEV + LK test the acid consumption was 322 sulfuric acid per t ore. Calculated acid consumptions in direct leaching was 400–500 kg sulfuric acid per t ore for LAI and LEV laterites and 900 kg sulfuric acid per t ore for LK laterite. Reduction of acid consumption and iron concentration is significant. Furthermore, the obtained acid consumptions are competitive to those in Komnitsas et al.'s [13] column leaching tests for Agios Ioannis ore, which is lower in Ni grade. Their acid consumptions were 0.69–0.76 kg sulfuric acid per 1 kg ore, when nickel extractions were 60.2–73.5 %.

**Table 8.** Cumulative acid consumptions (H<sub>2</sub>SO<sub>4</sub> kg/t dry ore) from H<sub>2</sub>SO<sub>4</sub> leaching of LAI (24 h) and LEV (6 h) laterites under the following conditions: pH 0.75, 90 °C, S/L = 30%, followed by LK addition to increase pH to 1.8 (until 48 h).

Laterite	pH	Time, h	H <sub>2</sub> SO <sub>4</sub> kg/t Dry Ore
LAI	0.75	24	565.25
LAI + LK	1.8	48	369.69
LEV	0.75	6	481.71
LEV + LK	1.8	48	421.94

At the end of the precipitation phase, iron yield to solution in the LAI + LK test was 1.4%, and in the LEV + LK test it was 2.8%. However, nickel yield to solution was not as high in the combined leaching and iron precipitation tests as in direct acid leaching of the laterites. The iron precipitation as jarosite in the LEV + LK and LAI + LK tests was verified by XRD analysis from the leach residues. The XRD analyses showed that iron was precipitated as sodium jarosite (NaFe<sub>3</sub>(SO<sub>4</sub>)<sub>2</sub>(OH)<sub>6</sub>) in both cases. Based on the calculations in Table 3, it is assumed that the major acid-consuming element in the

two-stage leaching approach is aluminum. This is consistent with the fact that iron precipitated as sodium jarosite and not sodium alunite.

Leach residues contained also iron oxides, gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ), and quartz ( $\text{SiO}_2$ ). Hematite was the main form of iron oxide, but some goethite was found from the leach residue of the LAI + LK leaching test.

This study's aim was to investigate the simultaneous nickel leaching and jarosite precipitation as a phenomenon. The overall aim was to improve the feasibility of atmospheric acid leaching by combining different types of laterites and specifically using a low-grade silicate laterite for neutralization. Using a low-grade laterite for neutralization decreases the need for limestone to enable iron precipitation, while also dissolving some additional nickel from the low-grade laterite. This study is the first step in the laterite process development project and the results presented here will be used for designing a pilot test run. In future research, the feasibility of the process will be further investigated. The aim is to find process conditions, which allow maximizing nickel yield while minimizing acid consumption and final iron concentration in the pregnant leach solution.

#### 4. Conclusions

A process involving atmospheric acid leaching of nickel laterites and simultaneous iron precipitation was investigated for the treatment of Greek LAI, LEV, and LK laterites. It was observed that iron control is possible when nickel leaching is combined with jarosite precipitation. These tests involved two steps, namely, (i) acidic leaching of LAI or LEV laterite at pH 0.75 and (ii) leaching of nickel from LK laterite in higher pH with simultaneous iron precipitation as jarosite. The aim of the jarosite precipitation is to decrease iron concentration in the leaching solution and at the same time to use the acid generated from the iron precipitation to obtain a higher nickel dissolution.

Atmospheric acid leaching tests of LAI, LEV, and LK laterite samples in 8 h experiments showed that pH lower than 1.5 was needed to effectively dissolve Ni from LAI and LEV, while Ni dissolved from LK already at pH 1.5. The potential for combined nickel leaching and iron precipitation was observed after 8 h of leaching. Based on the results, combined leaching and precipitation tests were planned. Tests began by leaching LAI (24 h) or LEV (6 h) laterites at pH 0.75, followed by increasing pH to 1.8 by LK laterite addition.

Acid consumption of atmospheric laterite leaching was high and the 8 h leaching tests showed that approximately 600–800 g acid per 1 kg laterite was needed for the Greek laterite samples LAI, LEV, and LK for an efficient nickel dissolution. The combined leaching and precipitation process has a potential to reduce acid consumption and decreased iron removal costs. Consumptions were 0.37 kg sulfuric acid per 1 kg for the LAI + LK test and 0.42 kg sulfuric acid per 1 kg for the LAI + LK test. Iron concentration decreased from 10 g/L to approximately 2–3 g/L during the jarosite precipitation stage. That indicates significant savings in iron removal costs since, in the conventional process, all dissolved iron has to be precipitated out from the leach solution using lime or limestone.

**Author Contributions:** V.M. and L.R. designed the experiments and critically analyzed the results. E.K. and V.M. provided industrial insight to the study. J.M. performed the literature review for the paper. L.R. supervised the carrying out of the experiments. T.K. studied the mineralogy of the samples. V.M. and L.R. wrote the paper in cooperation with the co-authors.

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