
Ferronickel slag produced in New Caledonia: characterisation and carbonation in seawater

Jordan Prévot

Laboratoire des Sciences Exactes et Appliquées (ISEA EA7584),
Université de la Nouvelle-Calédonie,
BP R4, 98851 Nouméa Cedex, New Caledonia
Email: jordan.prevot59@gmail.com

Arnaud Serres*

Laboratoire des Sciences Exactes et Appliquées (ISEA EA7584),
Université de la Nouvelle-Calédonie,
BP R4, 98851 Nouméa Cedex, New Caledonia
and
Laboratoire des Sciences de l'Ingénieur pour
l'Environnement (LaSIE UMR CNRS 7356),
Pôle Sciences et Technologie,
La Rochelle Université,
Avenue Michel Crépeau, 17042 La Rochelle Cedex 1, France
Email: arnaud.serres@unc.nc
*Corresponding author

Peggy Gunkel-Grillon

Laboratoire des Sciences Exactes et Appliquées (ISEA EA7584),
Université de la Nouvelle-Calédonie,
BP R4, 98851 Nouméa Cedex, New Caledonia
Email: peggy.gunkel-grillon@unc.nc

René Sabot and Marc Jeannin

Laboratoire des Sciences de l'Ingénieur pour
l'Environnement (LaSIE UMR CNRS 7356),
Pôle Sciences et Technologie,
La Rochelle Université,
Avenue Michel Crépeau, 17042 La Rochelle Cedex 1, France
Email: rene.sabot@univ-lr.fr
Email: marc.jeannin@univ-lr.fr

Abstract: Ferronickel slags (FNS) have been studied for a potential use of this industrial waste in seawater through mineral carbonation. Leaching tests have been performed using seawater and EDTA, a strong chelating agent. In both cases, only small concentrations (in the range of $\mu\text{g/g}$) of released heavy metals are measured by inductively coupled plasma, demonstrating the

non-hazardousness of FNS. The carbonation process of FNS was then observed by immersing them in artificial and natural seawater tanks for respectively four and seven months. FNS surface and cross-section samples have then been observed by scanning electron microscopy and chemical analysis. After seven months, a 5 cm thick sturdy conglomerate, composed of FNS stuck by a 25 μm thick calcium carbonate layer, is obtained. A mechanism of this natural carbonation process is proposed in the light of CO_2 sequestration.

Keywords: ferronickel slags; FNS; mineral carbonation; waste valorisation; metals leaching; CO_2 sequestration; New Caledonia.

Reference to this paper should be made as follows: Prévot, J., Serres, A., Gunkel-Grillon, P., Sabot, R. and Jeannin, M. (2022) 'Ferronickel slag produced in New Caledonia: characterisation and carbonation in seawater', *Int. J. Mining and Mineral Engineering*, Vol. 13, No. 1, pp.76–91.

Biographical notes: Jordan Prévot started his PhD project in 2016 after obtaining his Master's in Chemistry and Materials Engineering. His work was focused on the formation process and the physico-chemical characteristics of a conglomerate composed of the calcareous deposit and slags obtained after a pyrometallurgical process. He received his PhD at the University of New Caledonia in December 2020.

Arnaud Serres is an Assistant Professor in Material Sciences at the ISEA Laboratory (EA7484, UNC) at University of New Caledonia since 2008. His research is focused on the influence of the environment on the formation of materials at the mesoscopic scale and their properties. He is involved in projects related to the characterisation and the understanding of the formation of marine corrosion products and protection methods by-products such as the calcareous deposit.

Peggy Gunkel-Grillon after obtaining her PhD in 2001, she has occupied several teacher and researcher positions before becoming an Assistant Professor in 2008 at the University of New Caledonia in Environmental Chemistry. She is the Head of the ISEA Laboratory (EA 7484, UNC) since 2017. Her research interests concern metallic elements naturally present in the environment and the disturbance of their biogeochemical cycles by human activities.

René Sabot is an Assistant Professor in Chemistry at the LaSIE Laboratory (UMR CNRS 7356) at La Rochelle University since 1994. He has a huge experience in fields such as the corrosion and biocorrosion of metallic structures in the natural environment, the protection methods and the by-products formed and local electrochemical techniques.

Marc Jeannin is an Assistant Professor in Material Sciences and Spectroscopy at the LaSIE Laboratory (UMR CNRS 7356) at La Rochelle University since 1995. He is a specialist of the Raman μ -spectroscopy applied to metallic corrosion and biocorrosion in a marine environment. He also takes part in the study of the consequences of the cathodic protection processes and their possible technological uses.

1 Introduction

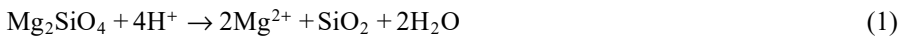
Nickel-containing products play an important role in our daily lives. If nickel is an important metal used in a wide range of applications, it is mostly exploited for the production of stainless steel (Arai et al., 1990). Two main industrial processes are followed to extract nickel from ore: a hydrometallurgical process and a pyrometallurgical process. At the end of the latter, a huge amount of a by-product is obtained: ferronickel slags (FNS). As an industrial waste, the storage of FNS is a common issue of this industry, as it has been underlined in China (Beidou et al., 2018). Finding reusable ways for FNS is then a challenge, depending on the different types of slags (Wu et al., 2018; Geiseler, 1996).

Among the different opportunities, FNS have shown interesting properties when used in the construction industry. They have been previously studied in cement plants as clinker (Ochida, 1984), and Saha and Sarker (2017) and Saha et al. (2018) demonstrated its good binding properties in concrete, as the compressive strength of mortar is maximised when 50% of sand is replaced by FNS during the concrete production.

New Caledonia owns 25% of the world available reserve of Nickel extractible ores (Kowasch, 2018), and the nickel production rate has been increasing over the years, reaching a peak nowadays [200 ktons/year in 1950, 800 ktons/year in 1985, 2,200 ktons/year in 2015 (BRGM, 2016)]. As a consequence, the main Nickel producer in New Caledonia, the ‘Société Le Nickel’ (‘SLN’) Eramet Company, produces up to 1.2 million tons of FNS per year (Augé, 2016). As a very small fraction of FNS is being used in applications such as backfill, road sub-layer materials, building construction or in the formation of artificial grounds to claim land offshore the New Caledonian archipelago, the large majority of FNS produced has been stored on the industrial site up to now. The consequence has been the creation of a huge artificial hill over the years, becoming a space occupation issue that still has to be addressed on the small island that is New Caledonia.

In the context of climate change related to the effect of greenhouses emissions, an alternative use of FNS concerns the CO₂ sequestration as highlighted by Seonhye et al. (2016). Due to the presence of Magnesium and Calcium silicates, slags are known to react naturally in seawater with CO₂ by a mineral carbonation process on the grains surface (Zevenhoven and Fagerlund, 2010; Rackley, 2017). CO₂ sequestration has also been studied on steel slag (Diener et al., 2010; Yadav and Mehra, 2017) with similar results.

The dissolution of ambient CO₂ in seawater leads to the acidification of seawater through the carbonic equilibrium with protons generation. The consequence is the dissolution of silicate present on FNS surface, leading to the release of metallic ions Mg²⁺ or Fe²⁺ and Silicon dioxide [equations (1) and (2)]:



Consumption of protons leads to an increase of the interfacial pH close to slags grains surface, inducing the precipitation of calcium carbonate [equation (3)] with calcium ions naturally present in seawater:



Carbonate precipitation at the FNS surface uses CO_3^{2-} anions resulting in the sequestration of dissolved CO_2 (Bodor et al., 2013). If FNS are immersed in seawater, the carbonates precipitation could be a mitigation path for oceans acidification (Iglesias-Rodriguez, 2013; Howes, 2015).

In this paper, the objective is to assess the mineral carbonation of FNS produced in New Caledonia for a potential valorisation and uses such as controlled embankment reinforcement and/or marine protection. To reach this purpose, FNS physical properties and their chemical behaviour in seawater have been studied.

FNS grains size distribution has been determined by a sieving process. The chemical composition has been determined with inductively coupled plasma (ICP-OES) analysis after a dissolution. X-ray diffraction (XRD) and μ -Raman spectroscopy were used to identify the mineralogy. Batch-leaching protocols have been followed to assess the potential release of toxic elements such as nickel or chromium as they are still present in FNS.

Finally, the mineral carbonation of FNS has been observed in natural and artificial seawater for several durations. Scanning electron microscopy (SEM) coupled with energy dispersive spectroscopy (EDS) and μ -Raman spectroscopy has been performed on slag grains after immersion to detect the presence of prospective carbonates. In order to find ways of recycling this industrial waste, a compression test on a natural agglomerate composed of FNS and carbonates formed in seawater has been performed, thus assessing the mechanical properties of such material that could be used in civil engineering if those properties are found to be adequate.

2 Materials and methods

2.1 Slag production and sampling

The specific FNS studied in the present paper is a by-product of the pyrometallurgical extraction process of Nickel from ores used by the 'SLN' Eramet plant, located in Noumea, New Caledonia, an archipelago located in the South-west Pacific Ocean (20–23°S). The ore, extracted from the New Caledonian ultramafic soil, is a result of the decomposition of a primal magnesian olivine (Mg, FeSiO_4) in the parent rock into clays and phyllosilicates under the tropical wet environment, forming nickel-bearing laterite and garnierite (Elias, 2002). In the industrial process, the ore undergoes an electric reduction between carbon electrodes in a furnace (Diaz et al., 1988; Bergman, 2003). Temperatures over 1,600°C are reached and the ore melts into two immiscible phases (Crundwell et al., 2011): a light one contains oxides of every metal that has not been reduced and forms the FNS, and a heavy one containing sulphurised compounds of Ni and Fe. This heavy phase is desulphurised, refined to remove the remaining oxides and hydrates, and finally cooled to obtain metallic ferronickel granulates composed of iron and nickel in 75%/25% ratio as chosen by the 'SLN' company (Ochida, 1984).

The by-product consists in the lightest phase that contains every compound that is not reduced; among them one can find silicon, magnesium, iron, and aluminium. This liquid phase is quenched through a seawater squirt, leading to the precipitation of the FNS, a mostly vitreous compound containing ferromagnesian silicates mineral (Ochida, 1984). It is finally stored on the industrial site close to the plant (22°15'2.759"S;

166°26'55.394"E). FNS used in this study have been collected from the industrial storage field.

2.2 *Microscopic and spectroscopic observations*

Semi-quantitative analysis of the FNS surface was performed by SEM using a JEOL JSM-IT 300 LV apparatus coupled with an EDS Oxford CAM 80 device.

μ -Raman spectroscopy was performed with a Jobin Yvon High Resolution Raman spectrometer (LabRAM HR-Evo) equipped with a microscope (Olympus BX 41) and a Peltier based cooled charge coupled device (CCD) detector. The analysed zones (diameter of 3 μ m) were observed at a magnification of $\times 50$. Spectra were recorded with the acquisition LabSpec software at room temperature with a resolution of 0.4 cm^{-1} . Excitation was provided by a green diode laser (532 nm). The acquisition time was then generally short (1–2 min) and each phase were identified via at least 10 Raman spectra.

2.3 *FNS characterisation*

2.3.1 *Texture*

The particle size distribution has been determined by a sieving method according to the EN 933-2 norm. Measures were performed in a wide range of sieves, from 0.063 mm to 4 mm. The particle size distribution curve is obtained by drawing the cumulative volume in percentage according to sieve diameters. Main information is the D50 value, which represents the particle diameter that 50% of the sample mass is smaller than and 50% of the sample mass is larger than.

Density is measured based on Archimedes thrust taking into account the porous nature of the material. Relative density is calculated by simply filling an empty container with an amount of slag, weighting the mass of slag and dividing the mass by the container volume.

The two characteristics above have been determined on FNS in ambient conditions of pressure (1 atm) and temperature (25°C) in order to estimate the void space between FNS grains that could be ultimately filled by the mineral carbonation. This void space is simply calculated by dividing the relative density by the density.

2.3.2 *Chemical composition and mineralogy*

FNS was dissolved by Lithium fusion prior to the chemical composition analysis in triplicates. A mass of 0.1 g of FNS is mixed with 0.5 g of lithium tetraborate in a crucible, which is placed in a furnace heated at 1,100°C for few minutes. After heating, the mixture forms a pearl that is dissolved into an acidic solution (4 mL of HCl 36% in 45 mL of water).

The solution is then analysed with a Varian 730ES inductively coupled plasma optical emission spectrometer (ICP-OES). Elements quantified using their respective wavelengths are, in nm: Al (394.4), Ca (317.93), Cr (267.71), Fe (234.35), Mg (280.27), Mn (260.56), Na (568.82), Ni (231.15), Si (288.15) and Zn (206.20).

The mineralogy has been determined by XRD with an INEL apparatus composed of a curved position sensitive detector CPS 120 and using a Cobalt $K\alpha$ radiation source. The

phases identification was performed based on the RUFF Database and the crystallography open database using the Match 2 (crystal impact) software.

2.3.3 FNS leaching experiments

To evaluate the hazardousness of FNS in the environment, two different leaching experiments have been considered. The first one was performed by immersing FNS in a solution of ethylenediaminetetraacetic acid (EDTA), which has been chosen for its powerful chelating property ($\log K(\text{Ni}^{2+}) = 18.4$; $\log K(\text{Zn}^{2+}) = 16.5$) (Harris, 2016). The use of EDTA induces the transfer of all extractable metals contained in FNS into the solution, thus allowing the evaluation of the concentration of potentially toxic metals that could be released over time in a worst case scenario. The EDTA extraction protocol was performed in 8 replicates: 3 mg of FNS has been immersed in a 30 mL solution of EDTA 0.05M, $\text{pH} = 6.5 \pm 0.05$ for 24 hours (Pasquet et al., 2018). This duration was chosen after performing preliminary tests where extracted metals concentration did not vary anymore.

The second set of FNS leaching experiments was performed in artificial seawater to simulate the natural environment. Duplicates were considered: 30 mg of FNS have been immersed in 1,000 mL of seawater at $\text{pH} = 8.2 \pm 0.05$ for 2,688 hours (four months).

In both sets, solutions were stirred at 500 rpm during leaching, and at the end of the experiment, they were centrifugated and filtrated by cellulose acetate filters of $0.45 \mu\text{m}$. Metals concentration transferred to the solution was finally determined by ICP-OES analysis.

2.3.4 Point of zero charge PZC

As the carbonation process occurs at the FNS/seawater interface, the charge state of FNS surface has been determined by measuring the PZC to evaluate the electrostatic effect on the surrounding ions involved. When the PZC is known, one can determine the sign of electric charges on the FNS surface by comparing to the pH of the solution: if the pH is higher than the PZC, charges will be negative (thus attracting positive ions); otherwise charges will be positive.

The technique consists in a pH titration of a HNO_3 0.03M solution containing different mass concentrations of FNS (5, 10 and 20 g/L) and a control solution without FNS, designated as 'blank' (Vakros, 2002; Cardenas-Peña et al., 2012). Triplicates of this protocol have been done and low mass concentrations have been chosen in order to limit the reactivity of slag in aqueous solution. Titrating solutions used were basic: NaOH 0.05 and 0.01M solutions. The PZC corresponds to the pH point where all curves obtained for FNS solutions cross the one corresponding to the blank solution.

2.4 FNS carbonation

2.4.1 FNS aging in artificial and natural seawater (in situ)

To understand the carbonation process on FNS surface, their reactivity in two different types of seawater has been evaluated.

Artificial seawater has been used as a control for the observation of calcium carbonate precipitation. It has been prepared by following the American Society of

Testing Material norm ASTM D1141. Two sets of artificial seawater have been synthesised: classic artificial seawater with calcium ASW + Ca($[Ca^{2+}] = 380 \text{ mg.L}^{-1}$) and artificial seawater without calcium ASW-Ca in order to evaluate the influence of the Calcium ion concentration on the carbonation process. In the case of ASW-Ca, $CaCl_2$ concentration was replaced by KCl in order to maintain the conductivity of the artificial seawater constant.

A mass of 200 g of FNS has been immersed in 1 L of artificial seawater. The solution was then covered to limit evaporation and solutions were not agitated. Seawater levels were maintained constant by adding deionised water to keep the volume constant. FNS immersion time was 4 months for both type of artificial seawater.

In natural seawater, aging has been performed in the Caledonian lagoon ($22^{\circ}15'40.274''S$; $166^{\circ}24'16.252''E$). A mass of 3,000 g of FNS packed in a meshed bag ($\varnothing = 40 \mu\text{m}$) to allow the seawater flow has been immersed in natural seawater for seven months.

2.4.2 Naturally agglomerated block of FNS

As FNS has been widely used in New Caledonia for a long time in civil engineering, a naturally agglomerated block of FNS has been collected on a free-access beach near a FNS backfilled area ($22^{\circ}16'0.0377''S$; $166^{\circ}24'49.078''E$). Even if the age of the sample cannot be determined, it can still be used as a control sample formed *in situ*.

A mechanical test was performed on the natural conglomerate ($80 \text{ mm} \times 80 \text{ mm} \times 50 \text{ mm}$). As the sample looked similar to concrete, a compression test has been performed according to the NF EN 12390-3 norm after polishing its surface: a preload of 20 N is applied, then the load speed is 50 mm/min.

3 Results and discussion

3.1 FNS texture and chemical composition

The D50 of slags is determined close to 1.1 mm, and according to Wentworth (1922) scale, it can be classified in the very coarse sand class. The measured density and relative density are respectively $2,700 \text{ kg.m}^{-3}$ and $1,600 \text{ kg.m}^{-3}$. From these values the void space is estimated to be around 0.4, meaning 40% of empty space is available in a known volume of FNS. Then, this high intergranular void volume between FNS grains could favour a good seawater flow and micro-chemical reactors between the mineral part and the solution.

The chemical analysis shows that FNS are mostly composed of Si (353 mg/g), Mg (213 mg/g) and Fe (103 mg/g) (Table 1). Due to the industrial extraction process, Iron and Nickel should not be detected in the FNS, but a small amount of these metals is still found, meaning it has not been totally reduced, and a part of FeO originating from the ore remains in the by-product. As Al, Cr and Mg are not desired in the final extracted product; they compose a large part of the FNS after the melting as they do not suffer from the reduction and remain under an oxide form (MgO , Al_2O_3 and Cr_2O_3). Na, Ni and Zn are present in small concentration (few mg/g). But it is not excluded that some of these elements could originate from seawater.

Table 1 FNS chemical composition expressed in mg/g ($n = 8$ replicates)

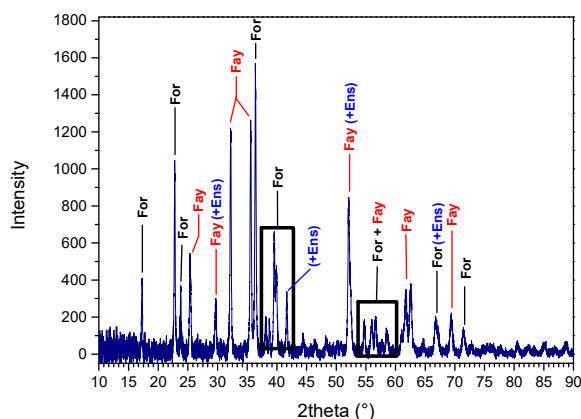
Element	Content (mg/g)
Al	18.0 ± 0.9
Ca	10.0 ± 0.6
Cr	10.0 ± 0.4
Fe	103 ± 4
Mg	213 ± 11
Mn	5.0 ± 0.3
Na	2.0 ± 0.2
Ni	1.0 ± 0.1
Si	353 ± 20
Zn	1.0 ± 0.1

Another source of these elements may also come from the quenching process used to form FNS. As the molten by-products are soaked in seawater in order to solidify, some elements present in seawater may crystallise in FNS grains.

3.2 FNS mineralogy

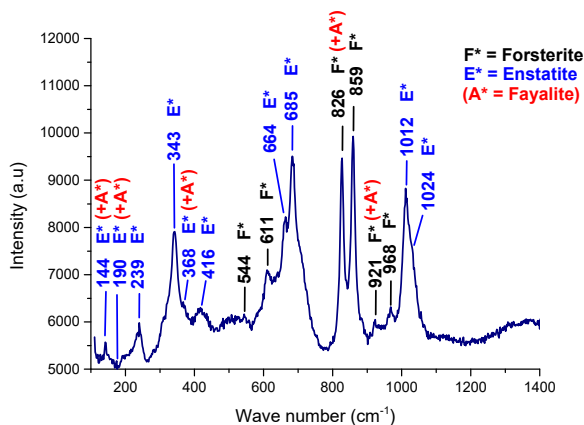
As FNS are mainly composed by a vitreous matrix of silicates, XRD patterns mainly exhibit an amorphous response. To observe the crystalline phases from the patterns, the amorphous phase has been evaluated and subtracted using the Match 2 software. Two crystalline phases have been identified (Figure 1). The main phase is composed by Olivine $\text{Mg}_{1.826}\text{Fe}_{0.174}\text{SiO}_4$, which is a mix of Forsterite (a magnesium pole Mg_2SiO_4) and Fayalite (a small ferric pole Fe_2SiO_4). The second phase is composed of Enstatite $\text{Mg}_{0.913}\text{Fe}_{0.087}\text{Ca}_{0.05}\text{SiO}_3$ where calcium is included in the mineral. As shown in Figure 1, Fayalite and Forsterite has been identified, and overlapped peaks of Enstatite have been indicated in parentheses.

Figure 1 XRD spectrum of FNS with peaks identification of Fayalite (Fay), Forsterite (For) and overlapped Enstatite (Ens) (see online version for colours)



μ -Raman spectroscopy measurements performed on the surface of FNS grains exhibit peaks of Enstatite and Forsterite according to their respective wave numbers (Figure 2). We observe a large amount of peaks of Enstatite at low wavenumber ($< 400 \text{ cm}^{-1}$), while Forsterite peaks are mainly regrouped between $500\text{--}970 \text{ cm}^{-1}$. Zhang et al. (2018) have performed Raman spectroscopy on Enstatite-rich meteorites, and we have found a very similar spectrum with negligible differences.

Figure 2 μ -Raman spectra of FNS with peaks identification of Enstatite (E*), Forsterite (F*) and Fayalite (A*) (see online version for colours)



This mineralogy analysis of FNS is consistent with previous compositions observed by Ochida (1984) for FNS obtained by a pyrometallurgical process.

3.3 Leaching results

FNS contain elements such as aluminium, chromium, iron, manganese, nickel or zinc, whatever the original ore (Bernardez and Andrade Lima, 2010; Mombelli et al., 2015; Potysz et al., 2015). These elements are potentially toxic for the environment if released in high concentrations under weathering and leaching conditions. In our case, the main elements extracted with EDTA leaching are silicon, magnesium and iron, with $288 \text{ }\mu\text{g/g}$ for Mg, $250 \text{ }\mu\text{g/g}$ for Si and $141 \text{ }\mu\text{g/g}$ for Fe (Table 2). This result was expected as these three elements are largely present in slags (see Table 1). But even though the extracting force has been greatly increased by using EDTA, the proportion transferred to the solution represents less than 0.14%. All other significant metals have the same behaviour, as only a small fraction of metals is released: manganese ($8 \text{ }\mu\text{g/g}$, 0.15%), nickel and aluminium, contents released with EDTA, are around $8 \text{ }\mu\text{g/g}$ that represents up to 0.83% for Ni but 0.15% for Mn and 0.05% for Al. Chromium and zinc concentration are respectively $4 \text{ }\mu\text{g/g}$ and $0.6 \text{ }\mu\text{g/g}$ that represents less than 0.06%. The proportion of heavy metals released by EDTA leaching, i.e., in a worst-case scenario of metals release by FNS, remains very low indicating that Mn, Ni, Al, Cr and Zn are not available in FNS.

In artificial seawater, concentrations of released elements after four months are very low. The main extracted elements are Mg with $94 \text{ }\mu\text{g/g}$ and Si with $10 \text{ }\mu\text{g/g}$ (Table 2). Fe, Ni, Mn and Zn extracted contents are respectively $0.20 \text{ }\mu\text{g/g}$, $0.16 \text{ }\mu\text{g/g}$, $0.33 \text{ }\mu\text{g/g}$ and $0.10 \text{ }\mu\text{g/g}$. The chromium concentration was too low to be detected by ICP-OES.

(< 0.015 µg/g). These results demonstrate that less than 0.04% of the total potential metallic contaminants are extracted in seawater after four months of immersion, and that except for Mg and Si, contents released in seawater are very low.

Table 2 Seawater and EDTA soluble elements in FNS after leaching (EDTA: $n = 8$ replicates for 24 hours; seawater: $n = 2$ replicates for four months)

<i>Elements</i>	<i>EDTA leaching</i>		<i>Seawater leaching</i>	
	<i>Content (µg/g)</i>	<i>% extracted/FNS</i>	<i>Content (µg/g)</i>	<i>% extracted/FNS</i>
Al	9.4 ± 0.5	0.05%	-	-
Cr	3.8 ± 0.2	0.04%	< 0.015	-
Fe	141 ± 7	0.14%	0.20 ± 0.01	0.00%
Mg	288 ± 14	0.14%	94 ± 9	0.04%
Mn	7.6 ± 0.4	0.15%	0.33 ± 0.01	0.01%
Ni	8.3 ± 0.4	0.83%	0.16 ± 0.01	0.02%
Si	250 ± 13	0.07%	10 ± 1	0.00%
Zn	0.6 ± 0.1	0.06%	0.10 ± 0.01	0.01%

As expected, the amount of metal released by seawater leaching is lower than what is extracted by using EDTA. The low values of metallic contaminants show the weak reactivity of FNS, meaning FNS may be used in seawater without any potential hazard.

Leaching tests in pH-static experiments have been previously performed on Brazilian FNS that have a similar composition to the ones studied in this article (Ettler et al., 2016). Researchers have demonstrated that even though a vitreous matrix mainly composes FNS, heavy metals could be released from a leaching due to seawater or rainwater. However contents released are low (few µg/g). Researchers have highlighted the concentrations of elements leached from Brazilian FNS in basic pH conditions, i.e., at $\text{pH} > 8$. When focusing on nickel and chromium, concentrations released are 0.3 µg/g and 0.15 µg/g, respectively. These concentrations are below the threshold limits for inert waste, according to the EU legislation (European Union, 2003): 10 µg/g for non-hazardous wastes, 40 µg/g for hazardous waste. Concentrations of other metals have been measured in FNS by Ettler et al. (2016): 3µg/g for Iron, 100 µg/g for magnesium, 80 µg/g for silicon.

3.4 Point of zero charge (PZC)

A first titration is performed with a 0.05M NaOH solution, and curves measured cross at a pH value around 8.5. Due to an important variation of the pH between 0.05 and 0.1 mL for the blank sample, a second titration has been performed with a 0.01M NaOH solution to smooth the curves and ensure a more accurate result. The PZC is found at 8.2, slightly lower than the value of about 9 reported in the literature for Fayalite and Forsterite (Ramachandra, 2004; Kosmuski, 2009).

The measured PZC for FNS is found to be very close to the value of pH for seawater (just below 8.2), but slightly higher. The FNS surface will then either carry neutral or positive charges, and as a consequence, negative ions such as carbonate ions will preferentially be attracted towards the surface, thus favouring the precipitation of calcium carbonate at the FNS surface.

3.5 Grain surface analyses after FNS aging in artificial seawater

At the end of the protocol described in section 2.4.1, the chemical composition of FNS surface was analysed by SEM-EDS. Results obtained in the case of each set of artificial seawater are reported in Table 3.

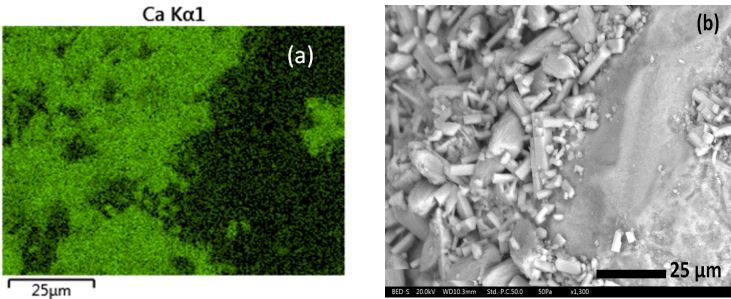
Table 3 SEM-EDS analysis for element content determination in weight percentage (W%) for the FNS surface: before immersion (control), after immersion in artificial seawater without Ca (ASW-Ca) or with Ca (ASW + Ca)

Element	Control (W%)	ASW – Ca (W%)	ASW + Ca (W%)
Al	3.9 ± 0.1	2.4 ± 0.1	1.2 ± 0.1
Ca	0.5 ± 0.1	-	12.8 ± 0.1
Cr	1.6 ± 0.1	1.1 ± 0.1	0.5 ± 0.1
Fe	16.1 ± 0.2	11.2 ± 0.1	5.8 ± 0.1
Mg	33.7 ± 0.3	22.5 ± 0.2	11.6 ± 0.1
Mn	0.9 ± 0.1	0.4 ± 0.1	0.3 ± 0.1
Si	43.2 ± 0.4	25.3 ± 0.3	13.5 ± 0.1

In the case of ‘ASW-Ca’, Si, Mg and Fe dissolution occurs since their content significantly decreases at the surface (Mg 22.5% instead of 33.7%; Si 25.3% instead of 43.2% and Fe 11.2% instead of 16.1%). This demonstrates that reactions according to equations (1) and (2) occur at the FNS surface.

At the end of the ‘ASW + Ca’ seawater experiment, grains surface analysis exhibits an important increase of the calcium weight percentage, from 0.5% for the control sample to 13%. As revealed by a SEM-EDS analysis of the surface (Figure 3), we can assume that CaCO_3 has formed on the slag surface. Moreover, crystals present in the form of small needles can be observed by SEM and identified as crystals of aragonite (Deslouis et al., 1998). The carbonate layer formed could also be thick enough to conceal the FNS surface from the detector, thus explaining the decreasing concentration of Al, Cr, Fe, Mg, Mn and Si.

Figure 3 (a) SEM images of a FNS surface in EDS mode and (b) BED-S (analysis of secondary electrons) mode (see online version for colours)

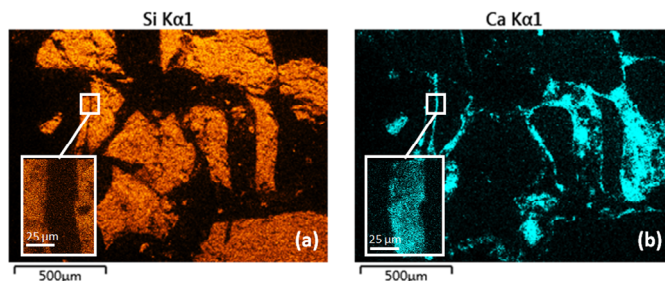


These results show the FNS carbonation process according to equation (3).

3.6 FNS aging in natural seawater

After seven months of aging in natural seawater, FNS have formed small brittle agglomerates of few centimetres and slag grains seem stuck together by a cement. In Figure 4, typical SEM-EDS elements maps of a cross-section of the agglomerate show calcium surrounding Si (representing FNS grains).

Figure 4 SEM-EDS pictures of a FNS agglomerate cross-section (see online version for colours)



Notes: Orange represents the silicon (FNS) and blue represents the calcium. Pictures A and B are zoomed area from upper pictures.

Calcium acts as a binder and traps slag grains, forming in the end agglomerates of FNS. Calcium content on Figure 4 has been estimated by EDS to be 13%W of the agglomerate and FNS elements (Si, Mg and Fe) to be 83%.

A zoom of the thinnest thickness between two grains of FNS demonstrates that 25 μm of Ca deposit is sufficient to bound two grains. This illustrates the binding role of a thin layer of calcium carbonate formed between two grains.

To understand the formation of the calcium carbonate layer, the following mechanism is proposed. The CO_2 dissolution in seawater leads to an acidification of the solution, causing the dissolution of slag grains at the FNS/solution interface according to equations (1) and (2). Due to this alkalisation close to FNS surface, the interfacial pH goes beyond the PZC, leading to two effects: 1-a negative charge state on the FNS surface, thus attracting cations such as Ca^{2+} ; and 2-an increase of the CO_3^{2-} concentration by a shift in the hydrogen carbonate/carbonate equilibrium. The conditions are then favourable to the formation of CaCO_3 according to equation (3). Even if Mg^{2+} are released by the FNS dissolution, MgCO_3 cannot be formed under our conditions (Hobbs and Xu, 2020). This mechanism may explain the natural conglomerate formed when immersing FNS in seawater.

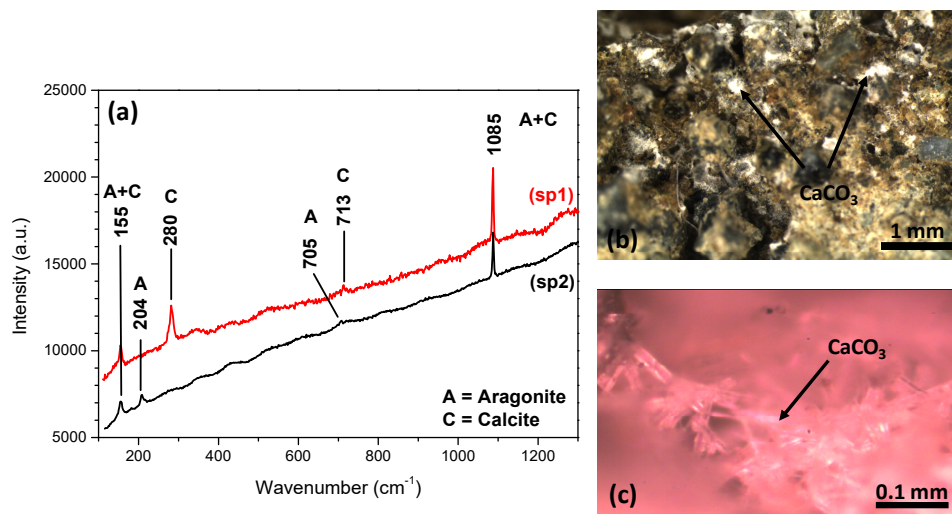
Considering that 1 mol CO_2 dissolved in seawater is used to form 1 mol CaCO_3 , a rough calculation on the amount of carbonates formed around the FNS grains shows that 1 g of FNS submersed in seawater could be used to trap 0.55g of CO_2 (Sanjuan and Girard, 1996).

3.7 Analyses on a natural block of FNS

The natural FNS conglomerate surface presents white deposits [Figure 5(b)] that have been analysed by μ -Raman spectroscopy [Figure 5(a)]. As the spectra shows, the deposits have been identified as the two allotropic forms of CaCO_3 : Aragonite (A), and calcite

(C). The picture on Figure 5(c) shows the CaCO_3 crystals representative of aragonite form.

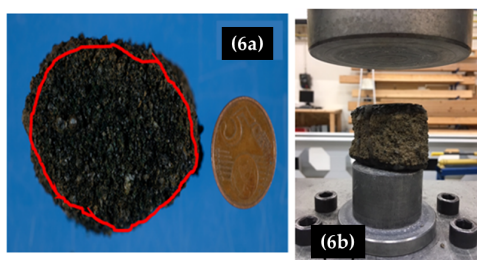
Figure 5 (a) μ -Raman spectra of carbonate layers on conglomerate surface after natural seawater aging with peaks identification of aragonite (A) and calcite (C), (b) calcium carbonate layers are identified on the right top picture by white marks on surface and (c) calcium carbonates crystals are observed on right bottom picture (see online version for colours)



Even if calcite is the most thermodynamically stable allotropic form (Elfil and Roques, 2001), in the presence of Mg^{2+} ions the aragonite allotropic form is favoured due to the Magnesium inhibiting effect on calcite's nucleation and growth (Barchiche et al., 2003; Morse et al., 2007). This explains the presence of the two forms of calcium carbonate and confirms the natural carbonation of FNS in presence of seawater.

A preliminary compressive test has been performed on the natural conglomerate, as shown on Figure 6. The pressure is applied on an area corresponding to a surface of around $1,480 \text{ mm}^2$ [perimeter of the contact surface in red, Figure 6(a)].

Figure 6 Natural sample used for the compression test, (a) in red, estimated perimeter of the surface contact, (b) sample placed in the device before compression (see online version for colours)



The measured strength to rupture of the block is 2052N, representing a compressive strength of 1.38 MPa. Even if this value is lower than a standard concrete with compressive strength range from 15 to 40 MPa (IAEA, 2002), the calcium carbonate acts

as cement around FNS grains and allows the formation of a mechanically resistant conglomerate in seawater. Thus, based on these preliminary results and their lack of hazardousness, another way of recycling FNS could be by integrating it in the formation of new materials used in civil engineering works such as seawater embankments.

4 Conclusions

Characterisation of FNS shows a particle size distribution with a D50 near 1.1 mm which is a value representative of a coarse sand. The granular compactness of 60% highlights the presence of void spaces between FNS grains, which could allow a precipitation on FNS surface.

FNS is mainly composed by a vitreous matrix of silicon dioxide, magnesium and iron. These elements form Forsterite, Fayalite and Enstatite, as we observed by XRD and μ -Raman analyses.

Even if the FNS chemical composition reveals small quantities of heavy metals (Cr: 10 mg/g; Ni and Zn: 1 mg/g), their possible release in the environment through leaching could become an issue when considering large amount of FNS. We have demonstrated that very low quantities ($< 10 \mu\text{g/g}$) of potentially toxic elements such as aluminium, chromium, nickel or zinc are released even in an aggressive environment as seawater or in the presence of a strong chelating agent, confirming that FNS are inert materials.

In addition to the releasing of Si, Mg and Fe, the leaching process in seawater induces an increase of the interfacial pH by the consumption of protons [equations (1) and (2)]. When combined with the PZC and the charge state on the surface, the formation of calcium carbonate is favoured. An immersion in artificial seawater confirms this process, as a thin layer of CaCO_3 after four months at FNS surface is obtained. A longer immersion in natural seawater gives small agglomerates of FNS grains bonded by a $25 \mu\text{m}$ thick layer of calcium carbonate. This phenomenon is rendered possible due to the important void between FNS grains.

The mineral carbonation of FNS in seawater could be a way of recycling this particular industrial waste by forming a new material with promising mechanical properties that is safe for the natural environment.

References

- Arai, H., Uchiyama, K., Matsumori, T. and Tohge, T. (1990) 'An economical process for stainless steel production from nickel ores', *Ferrous and Non-Ferrous Alloy Processes*, pp.1–14.
- Augé, T. (2016) '*Potential de piégeage du CO_2 par les scories de la pyrométallurgie du nickel*', CNRT, Nouméa.
- Barchiche, C., Deslouis, C., Festy, D., Gil, O., Refait, P., Touzain, S. and Tribollet, B. (2003) 'Characterisation of calcareous deposits in artificial seawater by impedance techniques III', *Electrochimica Acta*, Vol. 48, No. 12, pp.1645–1654.
- Beidou, X., Renfei, L., Xinyu, Z., Qiuling, D., Dingping, Z. and Wenbing, T. (2018) 'Constraints and opportunities for the recycling of growing ferronickel slag in China', *Resources, Conservation & Recycling*, Vol. 139, No. 41, pp.15–16.
- Bergman, R.A. (2003) 'Nickel production from low-iron laterite ores: process descriptions', *CIM Bulletin*, Vol. 96, No. 1072, pp.127–138.

- Bernardez, L. and Andrade Lima, L. (2010) 'Characterization of the heavy metals contamination due to a lead smelter in Bahia, Brazil', *Lead Zinc*, pp.917–927.
- Bodor, M., Santos, R.M., Van Gerven, T. and Vlad, M. (2013) 'Recent developments and perspectives on the treatment of industrial wastes by mineral carbonation – a review', *Central European Journal of Engineering*, Vol. 3, No. 4, pp.566–584.
- BRGM (2016) *Géosciences pour une terre durable*, Fiche de synthèse sur la criticité des métaux – Le nickel.
- Cardenas-Peña, M., Ibanez, J.G. and Vasquez-Medrano, R. (2012) 'Determination of the point of zero charge for electrocoagulation precipitates from an iron anode', *International Journal of Electrochemical Science*, Vol. 7, No. 7, pp.6142–6153.
- Crundwell, F.K., Ramachandran, V., Davenport, W.G., Moats, M.S. and Robinson, T.G. (2011) *Extractive Metallurgy of Nickel, Cobalt and Platinum Group Metals*, Elsevier.
- Deslouis, C., Festy, D., Gil, O., Rius, G., Touzain, S. and Tribollet, B. (1998) 'Characterization of calcareous deposits in artificial sea water by impedance techniques – I. deposit of CaCO_3 without $\text{Mg}(\text{OH})_2$ ', *Electrochimica Acta*, Vol. 43, Nos. 12–13, pp.1891–1901.
- Diaz, M., Landolt, C.A., Vahed, A., Warner, A.E.M. and Taylor, J.C. (1988) 'A review of nickel pyrometallurgical operations', *Extractive Metallurgy of Nickel & Cobalt*, Vol. 40, No. 9, pp.28–33.
- Diener, S., Andreas, L., Hermann, I., Ecke, H. and Lagerkvist, A. (2010) 'Accelerated carbonation of steel slags in a landfill cover construction', *Waste Management*, Vol. 30, No. 1, pp.132–139.
- Elfil, H. and Roques, H. (2001) 'Role of hydrate phases of calcium carbonate on the scaling phenomenon', *Desalination*, Vol. 137, No. 1, pp.117–186.
- Elias, M. (2002) 'Nickel laterite deposits – geological overview, resources and exploitation', *Giant Ore Deposits Workshop*, University of Tasmania, 17-19/06/2002.
- Ettler, V., Kvapil, J., Sebek, O., Johan, Z., Mihaljevic, M., Ratie, G., Garnier, J. and Quantin, C. (2016) 'Leaching behaviour of slag and fly ash from laterite nickel ore smelting', *Applied Geochemistry*, Vol. 64, No. T2, pp.1–10.
- European Union (2003) *Council Decision of 19 December 2002 establishing Criteria and Procedures for the Acceptance of Waste at Landfills Pursuant to Article 16 of and Annex II to Directive 1999/31/EC*, Official Journal of the European Communities.
- Geiseler, J. (1996) 'Use of steelworks slag in Europe', *Waste Management*, Vol. 16, Nos. 1–3, pp.59–63.
- Harris, C. (2016) *Quantitative Chemical Analysis*, 9th ed., W.H. Freeman & Co. Ltd.
- Hobbs, F.W.C. and Xu, H. (2020) 'Magnesite formation through temperature and pH cycling as a proxy for lagoon and playa paleoenvironments', *Geochimica et Cosmochimica Acta*, Vol. 269, pp.101–116.
- Howes, E. (2015) 'An updated synthesis of the observed and projected impacts of climate change on the chemical, physical and biological processes in the ocean', *Frontiers in Marine Science*, Vol. 2, p.36.
- IAEA (2002) *Guidebook on Non-Destructive Testing of Concrete Structures*, IAEA, Vienna.
- Iglesias-Rodriguez, M. (2013) 'Ocean acidification', *Earth System Monitoring*, pp.269–289, Springer.
- Kosmuski, M. (2009) *Surface Charging and Points of Zero Charge*, 1st ed., CRC Press, Boca Raton.
- Kowasch, M. (2018) 'Nickel mining in northern New Caledonia – a path to sustainable', *Journal of Geochemical Exploration*, Vol. 194, pp.280–290.
- Mombelli, D., Mapelli, C., Barella, S., Di Cecca, C., Le Saout, G. and Garcia-Diaz, E. (2015) 'The effect of chemical composition on the leaching behaviour of electric arc furnace (EAF) carbon steel slag during a standard leaching test', *Journal of Environmental Chemical Engineering*, Vol. 4, No. 1, pp.1050–1060.

- Morse, J., Arvidson, R. and Lüttge, A. (2007) 'Calcium carbonate formation and dissolution', *Chemical Reviews*, Vol. 107, No. 2, pp.342–381.
- Ochida, D. (1984) *L'utilisation des scories de Nickel de Nouvelle-Calédonie dans le génie civil*, Ecole nationale des ponts et chaussées, PhD thesis, Paris.
- Pasquet, C., Monna, F., Van Oort, F., Gunkel-Grillon, P., Laporte-Magoni, C., Losno, R. and Chateau, C. (2018) 'Mobility of Ni, Co, and Mn in ultramafic mining soils of New Caledonia, assessed by kinetic EDTA extractions', *Environ Monit. Assess.*, Vol. 190, No. 11, pp.638–650.
- Potysz, A., Kierczak, J., Fuchs, Y. and Grybos, M. (2015) 'Characterization and pH-dependent leaching behaviour of historical and modern copper slags', *Journal of Geochemical Exploration*, Vol. 160, pp.1–15.
- Rackley, R.A. (2017) '10 – mineral carbonation', in *Carbon Capture and Storage*, 2nd ed., pp.253–282, Butterworth-Heinemann, Elsevier.
- Ramachandra, R.S. (2004) *Surface Chemistry of Froth Flotation, Volume 1: Fundamentals*, Springer, New York.
- Saha, K. and Sarker, P.K. (2017) 'Compressive strength of mortar containing ferronickel slag as replacement of natural sand', *Procedia Engineering*, Vol. 171, pp.689–694.
- Saha, K., Khan, M.N.N. and Sarker, P.K. (2018) 'Value added utilization of by-product electric furnace ferronickel slag as construction materials: a review', *Resources, Conservation and Recycling*, Vol. 134, pp.10–24.
- Sanjuan, B. and Girard, J. (1996) *Review of Kinetic Data on Carbonate Mineral Precipitation*, BRGM.
- Seonhye, L., Ji-Whan, K., Soochun, C., Jun-Hwan, B. and Seung-Woo, L. (2016) 'CO₂ sequestration technology through mineral carbonation: an extraction and carbonation of blast slag', *Journal of CO₂ Utilization*, Vol. 16, pp.336–345.
- Vakros, J. (2002) 'Potentiometric mass titration: a quick scan for determining the point of zero charge', *Chemical Communications*, Vol. 17, pp.1980–1981.
- Wentworth, K. (1922) 'A scale of grade and class terms for clastic sediments', *The Journal of Geology*, Vol. 30, No. 5, pp.377–392.
- Wu, Q., Wu, Y., Tong, W. and Ma, H. (2018) 'Utilization of nickel slag as raw material in the production of Portland', *Construction and Building Materials*, Vol. 193, pp.426–434.
- Yadav, S. and Mehra, A. (2017) 'Experimental study of dissolution of minerals and CO₂ sequestration in steel slag', *Waste Management*, Vol. 64, pp.348–357.
- Zevenhoven, R. and Fagerlund, J. (2010) *Developments and Innovation in Carbon Dioxide (CO₂) Capture and Storage Technology, Carbon Dioxide (CO₂) Storage and Utilization*, Vol. 2, Woodhead Publishing.
- Zhang, B.R., Shieh, A., Withers, C. and Bouvier, A. (2018) 'Raman spectroscopy of shocked enstatite-rich meteorites', *The Meteoritical Society*, Vol. 53, No. 10, pp.2067–2077.