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Guiding mineralization process development with geochemical modelling

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Abstract

Mineralization is a CO_2 utilization solution that can possibly meet all the CO_2 mitigation criteria stated by the International Energy Agency, namely CO_2 emissions reduction, economic self-sufficiency and scalability. Considered as a global niche markets solution, mineralization process development is particularly challenging, as its scope is territory dependent and combines feedstock selection, mineralization technology and undisruptive product valorization through local materials supply chains. Identification of potential mineralization pathways is a definite challenge. This paper argues that geochemical modelling is an indispensable guiding tool for mineralization process development. Owing to its capacity to predict product speciation for complex mineralization systems, the paper discusses a number of issues that illustrate and confirm the value of geochemical modelling for feedstock selection, product valorization and process engineering. Supporting arguments are provided in the context of the valorization of Ni-slags from the New Caledonian metallurgical industry. It is concluded that geochemical modelling is an undisputed building block for developing and modelling any mineralization process. Moreover, the paper argues that the full potential of geochemical modelling for mineralization process design requires its merging with high-level decision-making frameworks, such as regionalized life cycle assessment.

Keywords: CO_2 utilization; mineralization; geochemical modelling; attrition-leaching; Ni-slags

1. Introduction

According to the IEA, CCUS will have to contribute 19% of the GHG emissions reductions needed up to 2060 in order to stay below the current 2°C climate change target [1]. This statement stresses that actual CCUS solutions are definitely needed, that they must be large scale solutions, and that their actual deployment must occur sooner rather than later. Deployment of large scale solutions over such a short time horizon also implies that eligible solutions must rely on proven industrial technology. Moving to the "U" component of CCUS, the IEA [1] states that worthy CO_2 utilization solutions must meet 3 criteria: (1) they must have the potential to achieve a significant emissions reduction, (2) they must generate revenue to offset their implementation costs, and (3) they must be scalable to scales commensurate with large point sources.

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Amongst CO_2 utilization options [2], mineral carbonation, also referred to as mineralization, appears to be the only CO_2 utilization solution that can meet all the above criteria. For many years, the development of mineralization as a CO_2 mitigation solution has been largely hindered by the fact that it was considered from a CCS (i.e. CCUS without the "U") perspective, leading to a biased service-to-service comparison with geological storage. Conclusions were therefore misleading and mineralization was labelled a niche and uneconomic solution to CO_2 mitigation by the CCS community. Notwithstanding the fact that mineralization does not just store CO_2 as it eliminates it, recent years have brought a completely different take on mineralization. It is now righteously described as a CO_2 utilization solution [2] that can produce useful commodities (e.g. construction and specialty materials, metals) while either eliminating CO_2 and/or reducing the carbon footprint of producing commodities by other means. The early criticism of mineralization being a niche solution has now become a strength. Indeed, as it has the potential to use CO_2 to valorize a wide variety of abundant natural and anthropogenic resources (e.g. mafic ores, brines, mining waste, metallurgical slags) into useful commodities, it can potentially process different feedstocks and therefore be deployed globally while being tailored to meet local markets. In other words, it can be tailored to valorize local feedstocks and produce materials that are needed locally also. Thus, mineralization can be described as a global niche markets solution and its economic and societal viability must be evaluated as such. Clearly, regional economic and LCA analyses must be used to guide the forms it should take locally. The need for scalability of mineralization solutions is technology dependent and must be met by the proposed mineralization solutions. The approach that is recommended by the authors is to develop solutions that rely upon proven technologies used by large-scale industries. This will not only ensure the scalability of the proposed solutions, but also their industrial acceptability and hence potential for rapid deployment.

The solution developed by the authors, which is described in the next section, has the potential to meet all these criteria. It does not preclude the need to develop many other solutions. Indeed, there is no one solution that fits all. Depending on local constraints, one mineralization solution may be more cost-effective than another, and the fact that mineralization can be implemented in different ways must be seen as an actual strength of this CO_2 utilization solution. The corollary is an implicit need to standardize the way by which one may be able to compare and select mineralization solutions. The ongoing work of ISO/TC265 to provide standard guidelines for conducting LCA analysis for CO_2 utilization solutions is important in this respect.

Nomenclature

CCUS	Carbon Capture, Utilization and Storage
IEA	International Energy Agency
GDP	Gross Domestic Product
GHG	Greenhouse Gases
ISO/TC265	Technical committee of the ISO standard on Carbon dioxide capture, transportation, and geological storage.
LCA	Life Cycle Analysis
P_{CO2}	CO_2 partial pressure (atm)
PSD	Particle Size Distribution
T	Temperature (°C)

2. Mineralization by attrition-leaching

The proof of concept of the mineralization process developed by the authors, which they refer to as "attrition-leaching", has been established [3,4]. Its development is currently pursued through a project supported by the New Caledonian Energy Agency (project ACE No. CS17-3160-00), whose aim is to produce materials that meet the needs of the construction sector in New Caledonia through mineralization of pyrometallurgical Ni-slags. Currently, CO_2 emissions per capita are about 25 metric tons per annum and expected to rise in New Caledonia, which is high by any standard. Moreover, the Ni mining and metallurgical industry, which accounts for 20% of the territory's GDP is blamed for half of these emissions. Beyond numbers, this is a cause of concern in terms of pollution in the capital, Nouméa, and measures are being taken to reduce this issue through modernizing industrial power production

systems. The Ni mining industry also produces about 3 million tons of Ni-slags per year as industrial waste. Considering the scale of the New Caledonian mining industry and its significance to the local economy, the favorable properties of Ni-slags as a mineralization feedstock, the insularity of the territory and the stunning beauty of this southwest Pacific island, this project combines many ingredients of a significant project on mineralization.

The attrition-leaching mineralization process falls in the category of hydrometallurgical processes. Moreover, it is of the direct aqueous mineral carbonation type. Indeed, it couples dissolution of the particulate feedstock in water acidified by dissolved CO_2 with precipitation of carbonates that bind cations (e.g. Mg, Fe, Ca) that are leached out of the feedstock with dissolved CO_2 species [5]. The rationale behind the attrition-leaching mineralization process is a continuous mechanical exfoliation of carbonatable feedstock particles during their leaching to offset the surface passivation that invariably plagues their leaching. It also coproduces fine particles of feedstock particles which is favorable in terms of reactive particle surface area. The authors developed this concept in a wet stirred media mill, whose technology is proven and accepted by large-scale mining operations throughout the world [6]. Tested on a number of natural Mg-bearing ores and mining waste, this mineralization solution was found to be largely insensitive to the nature of the feedstock. The extent of carbonation that has been obtained to date with this process under batch conditions can exceed 80% in 10 to 24 hours, starting with minus 100 µm feed particles.

The scope of the mineralization process, as described earlier, makes its optimization a complicated and possibly unintuitive matter. Indeed, optimization is not limited to standard process engineering, i.e. dealing with operating conditions such as CO_2 partial pressure, temperature, solid-liquid ratio and net energy consumption, as it must also account for the processing of local feedstocks to yield products that can contribute positively to the local supply chain of construction materials. This challenging objective goes beyond standard hydrometallurgical process optimization strategies used by process engineers.

Possibilities are virtually innumerable. Indeed, depending on the composition of the feedstock, nickel slags in this case, and the operating conditions used, a variety of product phases can be formed, whose value for producing added-value materials will depend on the local situation. Possible target materials may include hydraulic binders [7,8], fillers and pozzolanic materials, to name just a few possibilities depending on the local supply chain for construction materials.

There is a need for guiding tools to help narrow down the possibilities prior to designing the process and conducting actual experiments. One such tool is geochemical modelling [9], which is defined here as a modeling framework that predicts the evolution of the chemical composition of phases in the mineralization system, based on thermodynamic and kinetic models. Geochemical modelling can be a judge of peace for mineralization process design. Indeed, if geochemical modelling predicts that a phase of interest does not form under particular conditions, it cannot be expected to form in real life. However, geochemical modelling predicting the formation of a particular phase does not necessarily mean that it will form in real life, and experimentation is inseparable from geochemical modelling for mineralization process design.

Given the uncertainties or lack thereof of thermodynamic and kinetic data, geochemical modelling results provide trends only, hence the value of geochemical modelling as a "guiding" tool for process design and operation. In other words, geochemical modelling results should not be understood as absolute, i.e. they are no substitute for experiments for obtaining absolute process performance values. Nonetheless, the value of geochemical modelling for mineralization process design is invaluable. The next section illustrates some of the features of geochemical modelling for guiding the attrition-leaching mineralization process design.

3. Geochemical modelling as a guide for Ni-slags mineralization process design and operation

3.1. Geochemical model settings

The mineralization feedstocks of interest to the project are pyrometallurgical Ni-slags produced in New Caledonia. Fig. 1 positions these slags in a MgO-Fe_2O_3-SiO_2 composition diagram. In terms of mineralogy, Ni-slags can be regarded as ultramafic rocks, for which the attrition-leaching mineralization process has been found to work well, producing magnesite as the main mineralization product [3,4]. A typical molar composition of Ni-slags given

as metal oxides and limited to the principal metals is (SiO_2 1, MgO 0.824, Fe_2O_3 0.104, Al_2O_3 0.022). This is the composition used in the paper. It is noted that geochemical modelling can help quantify the effect of variations in composition, including minor elements such as Mn and Ca, which are also present in Ni-slags.

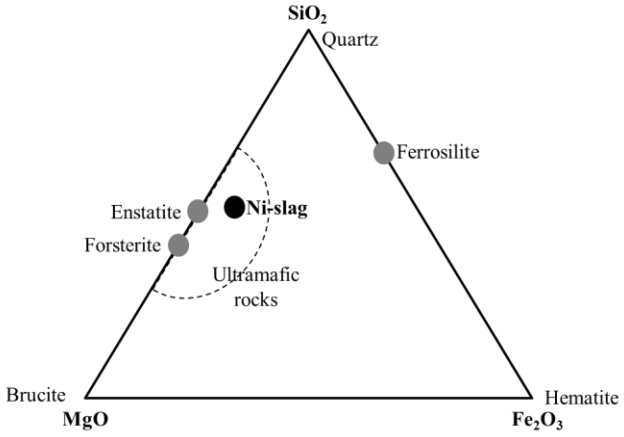


Fig. 1. Position of New Caledonian Ni-slags in the MgO-Fe_2O_3-SiO_2 composition diagram

Prediction of mineralization products is achieved with the geochemical modelling software PhreeqC [10]. The numerical calculations are carried out using the R interface package to PhreeqC [11]. Running the geochemical calculations in a numerical environment such as R makes it possible to seek process conditions that meet specific targets and carry out sensitivity analysis of process performance [12]. One value of geochemical modelling is to permit analyzing the sensitivity of the mineralization process to various process inputs, including:

- The composition of the feedstock, which can be modified to evaluate the effect of a minor element for example.
- The feedstock particle size distribution, which affects the surface-driven process kinetics.
- The process operating conditions, such as temperature and CO_2 partial pressure.
- The water composition, which can be varied to assess the possibility of using sea water for example.
- The nature of the grinding medium, which can possibly affect the process performance. Possibilities include using inert or reactive grinding medium [9], as well as testing the option of using autogenous attrition.

3.2. Inputs to the geochemical model for the attrition-leaching mineralization of Ni-slags

Applying geochemical modelling to mineralization process design requires feedstock specific properties (elemental and mineral composition as well as the particle size distribution (PSD)) combined with appropriate thermodynamic and kinetic models.

The thermodynamic model main features are as follows:

- The gas phase is an ideal mixture of CO_2, H_2O, CH_4 and H_2, each compound being described by the Peng-Robinson equation of state.
- The aqueous phase is described according to the LLNL aqueous model, which is a variant of the Debye-Hückel model (the so-called B-dot equation). This approach is fully justified by the low ionic concentration of the solution (ionic strength of about 10^{-3} to 10^{-2}).
- The solid phases are described as stoichiometric compounds, except for the $(Mg,Fe)CO_3$ solid solution which was modeled with a regular solution parameter of 4.44 $kJ.mol^{-1}$ at 770 K [13].

All model parameters (equilibrium constants and Debye-Hückel parameters for aqueous species) come from the 2017 version of the Thermoddem database [14] (downloadable at http://thermoddem.brgm.fr/).

Some knowledge about speciation pathways of the system is also necessary. For example, precipitation of silica as amorphous silica is favored over quartz, therefore precipitation of quartz is blocked in the geochemical simulation. The same applies to goethite, whose formation is favored over hematite and magnetite under mineralization

conditions. There is no substitute for comprehensive literature review and precise experimentation to tailor the geochemical modelling hypotheses to the mineralization system of interest. Validation of geochemical hypotheses is an iterative process, whereby questions are asked about the likelihood of formation of predicted phases and corrections made to the geochemical hypotheses depending on confirmation from literature and experiments.

The dissolution kinetics of the slag particles uses the model and associated parameters proposed by Oelkers and Schott [15] for enstatite. As seen in Fig. 1, this is a fair assumption even though it approximates the actual mineralogy of Ni-slag samples, which X-Ray diffractograms evidence the presence of forsterite (Mg_2SiO_4), enstatite ($MgSiO_3$) and ferrosilite ($FeSiO_3$). The dissolution rate r is given by:

$$r = k_0 e^{\left(-\frac{E_a}{RT}\right)} a_{(H^+)}^{0.25} a_{(Mg^{2+})}^{-0.125} \quad (1)$$

where $a_{(i)}$ is the activity of aqueous compound i, E_a the activation energy and R the gas constant.

To have a realistic dissolution rate model for the Ni-slag, the pre-exponential kinetic constant k_0 was adjusted against experimental measurements. This was achieved by matching the predicted CO_2 consumption of a Ni-slag sample having the PSD of Fig. 2 with that measured in a 300 mL attrition-leaching batch experiment conducted near 180°C with P_{CO2} = 20 atm [3]. Such an approach for kinetic model adjustment is imperfect, and yet it is deemed sufficient for exemplifying the potential of geochemical modelling as an orientation tool for attrition-leaching mineralization process design. Among its known flaws, the approach assumes that PSD changes due to dissolution only, i.e. particle attrition kinetics of the attrition-leaching process matches the particle dissolution rate exactly. It is likely that the actual particle attrition rate exceeds the dissolution rate, hence a probable overestimation of the real Ni-slag dissolution rate.

The PSD of Ni-slag particles produced by dry milling is well described by a Rosin-Rammler distribution. A typical PSD used in batch attrition-leaching mineralization tests is shown in Fig. 2 in cumulative surface percent passing, with a top size around 100 µm.

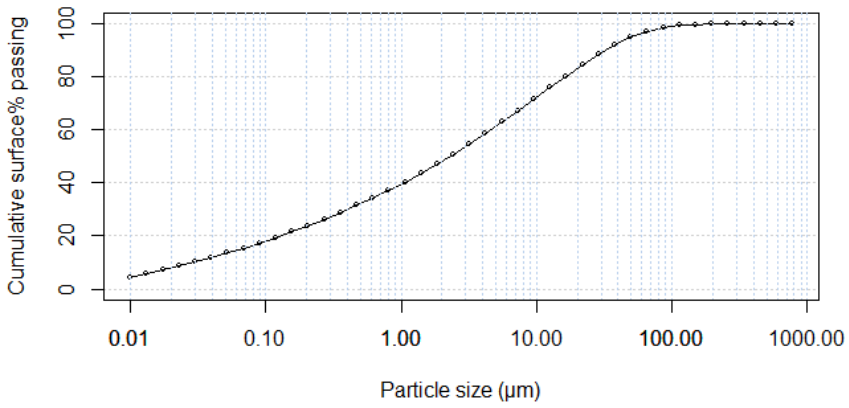


Fig. 2. Typical particle size distribution of Ni-slags for the mineralization process

The experimental PSD is specified to PhreeqC as a discretized surface PSD given the surface-driven nature of the mineralization process. Forty or more particle size classes are used in the simulation to describe the experimental particle size distribution. Each particle size class is input to the PhreeqC as a separate phase, all classes having identical chemical composition, thermodynamic and dissolution kinetic properties.

The time variation of the slag PSD is recalculated at each calculation time step, by conserving the number of particles in each size class and recalculating their size based on the mass loss during the time step. It is assumed that particle attrition kinetics matches the particle dissolution rate exactly. Future work plans to couple the geochemical dissolution model with an actual attrition model, using grinding models suitable for stirred mills. Investigation of the

actual attrition and leaching rates is an important aspect of attrition-leaching mineralization process optimization which has not yet been investigated.

3.3. Geochemical modelling as a guide to selection of attrition-leaching Ni-slag mineralization pathways

The attrition-leaching mineralization process must be optimized with respect to many variables, including time, energy and water consumption. However, given the paramount objective of producing phases that can enter the construction materials supply chain, the first question concerns the phases that can be formed by the attrition-leaching mineralization process of Ni-slags. To this end, CO_2 partial pressure and temperature were varied in the range [0.1-20] atm and [100-180] °C respectively in the geochemical simulations. It is noted that the authors use the conditions [20 atm; 180°C] as their base case for conducting mineralization experiments.

Across this range of conditions, geochemical modelling predicts that Ni-slags can produce numerous phases (See Table 1). Addition of minor elements such as Ca or Mn present in the Ni-slags yield additional phases.

Table 1. Mineral phases formation predicted by geochemical modelling for P_{CO2}= [0.1-20] atm and T= [100-180] °C

Phase type	Phase name	Formula
Carbonates	Magnesite (Synthetic)*	$MgCO_3$
	Siderite*	$FeCO_3$
Metal (hydr)oxides	Amorphous Silica	SiO_2
	Goethite	$FeO(OH)$
Magnesium silicates	Talc	$Mg_3Si_4O_{10}(OH)_2$
	Antigorite	$Mg_{48}Si_{34}O_{85}(OH)_2$
	Montmorillonite(HcMg)	$Mg_{0.3}Mg_{0.6}Al_{1.4}Si_4O_{10}(OH)_2$
	Sudoite	$Mg_2Al_4Si_3O_{10}(OH)_8$
	Chlinochlore	$Mg_5Al(AlSi_3)O_{10}(OH)_8$
	Beidellite(Mg)	$Mg_{0.17}Al_{2.34}Si_{3.66}O_{10}(OH)_2$
	Saponite(Mg)	$Mg_{3.17}Al_{0.34}Si_{3.66}O_{10}(OH)_2$
	Saponite(FeMg)	$Mg_{.217}FeAl_{0.34}Si_{3.66}O_{10}(OH)_2$
Other silicates	Minnesotaite	$Fe_3Si_4O_{10}(OH)_2$
	Chamosite.Daphnite	$Fe_5Al(AlSi_3)O_{10}(OH)_8$
	Pyrophyllite	$Al_2Si_4O_{10}(OH)_2$

** The two carbonates are described as a full (Fe,Mg)CO_3 solid solution*

From a product valorization standpoint, 4 families of phases are identified in Table 1, namely carbonates (whose dominating form is a Fe-enriched magnesite according to Rietveld analyses on experimental products), metal (hydr)oxides, Mg-bearing silicate phases (whose formation competes with the formation of magnesite) and other silicate phases. Some of these phases offer promising perspectives from a construction materials production perspective, whereas others may be less desirable depending on the application. Moreover, with the exception of amorphous silica for which thermodynamic data is described in the Thermoddem database, it is not possible to predict whether amorphous or crystallized aluminosilicates will form during the process. Experiments are needed to shed light on this issue for product utilization, given the higher reactivity and potential value of amorphous alumina silicate admixtures positive on concrete properties [16].

A sensitivity analysis was carried out with respect to the effect of the presence of Al in the Ni-slags. Indeed, geochemical modelling predicts the possibility of Al forming many silicate phases with Mg depending on its grade in the Ni-slags (See Table 1). With the stoichiometry used, the formation of talc and amorphous silica is predicted to occur. TEM petrographic analyses of Ni-slag mineralization product confirmed the formation of spherules and fluffy particles as talc. Geochemical modelling predicts a strong effect of Al in the slag, whose increase yields the formation of aluminosilicate phases instead of amorphous silica. This speciation has a direct bearing on possible product valorization, depending on the amorphosity of such phases.

The capacity of geochemical modelling to predict the effect of specific elements on product speciation is very powerful. Indeed, the first-hand prediction of product speciation provided by geochemical modelling is relevant for both feedstock mapping and product valorization. Geochemical modelling can be used to assess the value of local feedstocks, with or without blending, in relation to local needs for construction materials. Geochemical modelling can be used as resource mapping tool, and help define the range of feedstock compositions that one should prioritize for a particular product valorization purpose, especially if the formation of a specific phase must imperatively be avoided. Alternatively, given a feedstock, geochemical phase prediction can imply that specific separation steps must be taken to control the level of specific elements in the mineralization process.

Fig. 3 shows the predicted amount of leached Ni-slag as a function of temperature and CO_2 partial pressure for a 24 hour mineralization experiment with base case conditions. It is readily seen that higher temperature and CO_2 partial pressure yield a monotonic increase in the extent of reaction of Ni-slags. For process optimization, the downward slope of the iso-contours suggests that increasing CO_2 partial pressure permits reducing temperature for the same conversion of the Ni-slags.

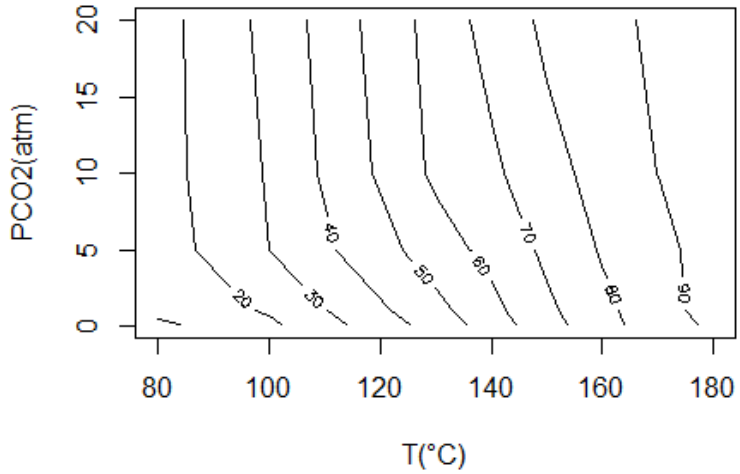


Fig. 3. Predicted Ni-slag dissolution extent as a function of temperature and P_{CO2}

Fig. 3 however does not say anything about the composition of the mineralization products. Figs. 4 and 5 show iso-contours for the predicted mass fraction of carbonates and amorphous silica in the mineralization product, both phases being of interest for product valorization as construction materials. The hand-drawn dotted lines show the locus of the most favorable ($T;P_{CO2}$) set points for maximizing the production of both product phases as predicted by geochemical modelling.

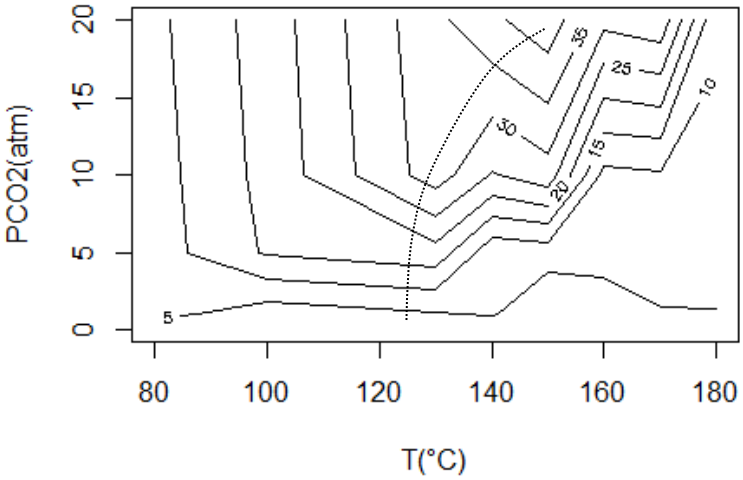


Fig. 4. Predicted mass percent of carbonates in mineralization product as a function of temperature and P_{CO2}

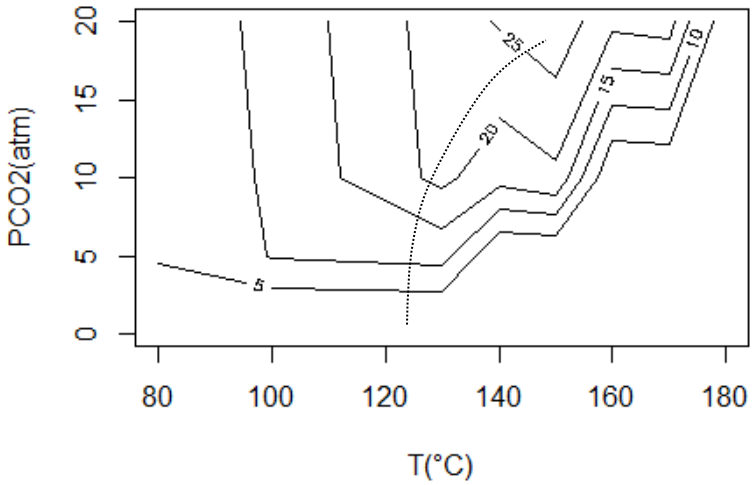


Fig. 5. Predicted mass percent of amorphous silica in mineralization product as a function of temperature and P_{CO2}

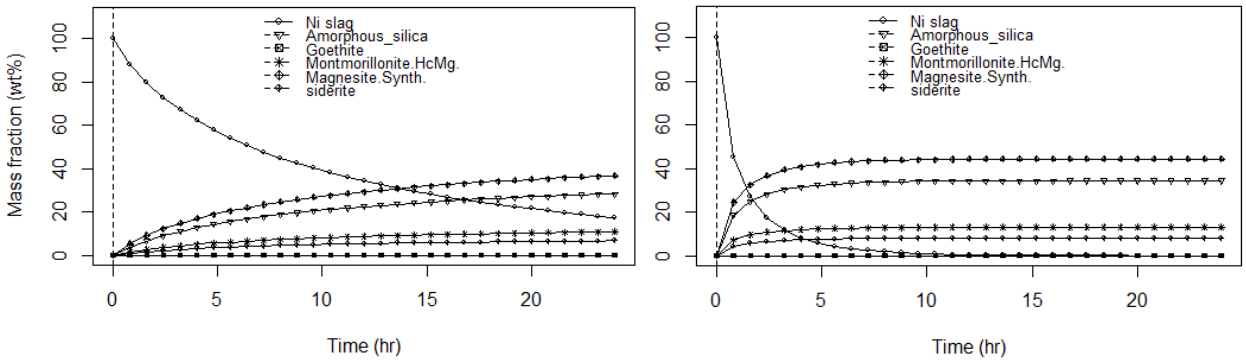
Should one want to promote the formation of these phases, geochemical simulations indicate that a temperature of 150°C is the best set point for a CO_2 partial pressure of 20 atm, for which Fig. 3 predicts a Ni-slag dissolution between 70% and 80%. The same analysis can be carried out for any potential phase of interest, providing the information needed by materials engineers to explore all possibilities for valorization of Ni-slags as construction materials.

3.4. Geochemical modelling as a guide to selection of attrition-leaching Ni-slag mineralization operating conditions

Once solutions for product valorization have been identified, geochemical modelling can then be used for process design. In the mineralization context, prediction of pH can be obtained, which is significant for process material selection. At a temperature of 150 °C and a CO_2 partial pressure of 20 atm, geochemical modelling predict a pH value of 5 using plain water. Other questions can be asked about the effect of many basic process variables, such as slurry concentration, which echoes with a lesser water consumption. Increasing solids concentration in the range 10 to 40 wt% is not expected to affect the product speciation according to the geochemical model. Nevertheless, increasing slurry concentration is critical from a process perspective, in terms of water footprint, downstream processing and conversion of products to construction materials. As the geochemical model reported here is not coupled with a grinding model, the kinetics of appearance of the product phases is not predicted to depend on concentration of solids in the slurry. This is not expected to hold true in practice as it surely affects stirred milling performance.

Prediction of process kinetics, in terms of leaching of Ni-slag and appearance of the phases of interest, is important for process design and performance. Here also, geochemical modelling can be of assistance. Fig. 6 shows the time-dependent formation of phases that are predicted to form as a function of feed particle top size.

Fig. 6 confirms the significance of the feedstock particle size on the process kinetics, which is valuable information for process design and optimization. With the attrition-leaching process, the rate of change of particle size depends both on Ni-slag leaching kinetics and attrition rate, which must be optimized as a whole. Fig. 7 shows the predicted rate of change of the Ni-slag PSD as a function of time, as predicted from shrinking particle dissolution kinetics only. It exemplifies the rapid disappearance of the finer particles driven by their high specific surface area.



(a) Particle top size = 100 µm *(b) Particle top size = 10 µm*

Fig. 6. Predicted mineralization product phases (T=150°C, P_{CO2}=20 atm).

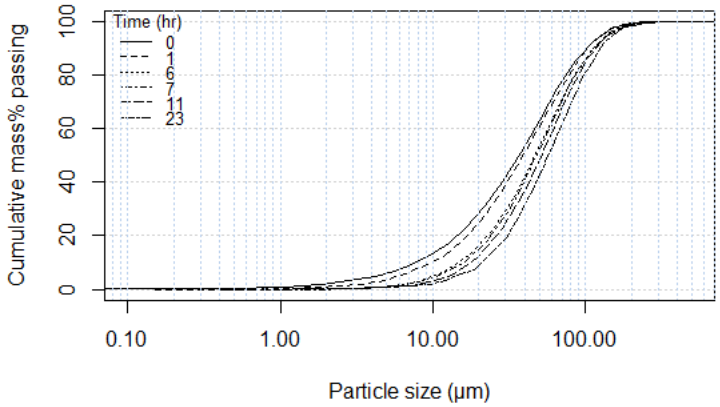


Fig. 7. Predicted rate of change of Ni-slag PSD during the mineralization process (T=150°C, P_{CO2}=20 atm)

Other more complex process parameters can be investigated by geochemical modelling, such as gas and water composition. When dealing with mineralization processes, the possibility of using flue gases, which carry low CO_2 partial pressure and possible minor elements, is important. Notwithstanding potential corrosion issues, the possibility of using sea water instead of fresh water as the aqueous medium also offers promising alternatives from an environmental standpoint. Indeed, sea water is already being used to quench molten slags in some New Caledonian pyrometallurgical plants and preservation of fresh water resources is paramount. Here also, geochemical modelling can help predict product speciation.

3.5. Final words on selection of attrition-leaching Ni-slag mineralization pathways with geochemical modelling

This paper has exemplified that geochemical modelling can provide valuable first-hand information on the effect of key variables on mineralization process design and optimization, from feedstock assessment to product valorization.

Although an invaluable guide for narrowing down possible mineralization pathways based on particular constraints, such as the formation of desirable phases for a local materials supply chain, geochemical modelling is not self-sufficient as a decision making tool. Geochemical modelling is deemed a key building block for mineralization process modelling, whose predictions can be used to feed actual decision-making tools. To harvest its full potential for mineralization process design, geochemical modelling must be coupled with supervisory frameworks that converts its predictions into environmental and economic units, using validated regionalized impact and value assessment methods. In particular, the authors see significant potential in integrating geochemical modelling into a regionalized LCA programming environment. With the scripting interface now available in openLCA version 1.7 [17] for example, there is a significant potential for interfacing LCA analysis with a geochemical metamodel that calls PhreeqC through R. This is the path the authors intend to pursue in order to deliver a decision-making tool for

tailoring the attrition-leaching mineralization process to produce low carbon footprint construction materials to regional markets using local feedstocks.

Conclusions

Mineralization is a promising CO_2 utilisation solution. In principle, it can meet the three CO_2 mitigation criteria set by the IEA, namely CO_2 emissions reduction, economic self-sufficiency and scalability. One promising mineralization process is the attrition-leaching process that is currently being applied for valorizing the Ni-slags produced by the New Caledonian metallurgical industry.

Mineralization process development is challenging as its scope is territory dependent and combines feedstock selection, mineralization technology and non disruptive valorization of mineralization products through local materials supply chains. Identification of potential mineralization pathways is a definite challenge, which starts with the complexity and variety of mineralization systems' geochemistry.

The paper argues that geochemical modelling as an indispensable tool for design of aqueous mineralization solutions. Using New Caledonian Ni-slags as feedstock, a large-scale and local industrial waste, the paper attempts to exemplify the capacity of geochemical modelling to predict product speciation in valuable mineralization systems. It is shown that geochemical modelling provides first-hand information critical to evaluation of both feedstock and product valorization potential. From a technological standpoint, geochemical modelling can also provide insightful information about the effect of important process operating variables on process performance.

Geochemical modelling is therefore an indisputable building block for developing and modelling any mineralization process. To harvest its full potential for mineralization process design, it is believed that geochemical modelling must be embedded into a supervisory framwork that converts geochemical model predictions into environmental and economic units, such as regionalized LCA.

As a last word of caution, if the potential of geochemical modelling is indisputable for mineralization process design, its potential depends strongly on the user's expertise and critical thinking. This point must never be underestimated, and it is certainly no substitute for dedicated experiments, which are indispensable for fine tuning geochemical model settings for s specific mineralization system. In the context of mineralization of Ni-slags by attrition-leaching, additional product characterization is necessary to confirm the predicted speciation, in particular about the formation of aluminosilicate phases and their amorphosity. Also, coupling geochemical modelling with a validated attrition model is required for further process development and optimization.

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Guiding mineralization process development with geochemical modelling

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Mineralization of CO_2

Mineralization in the international context

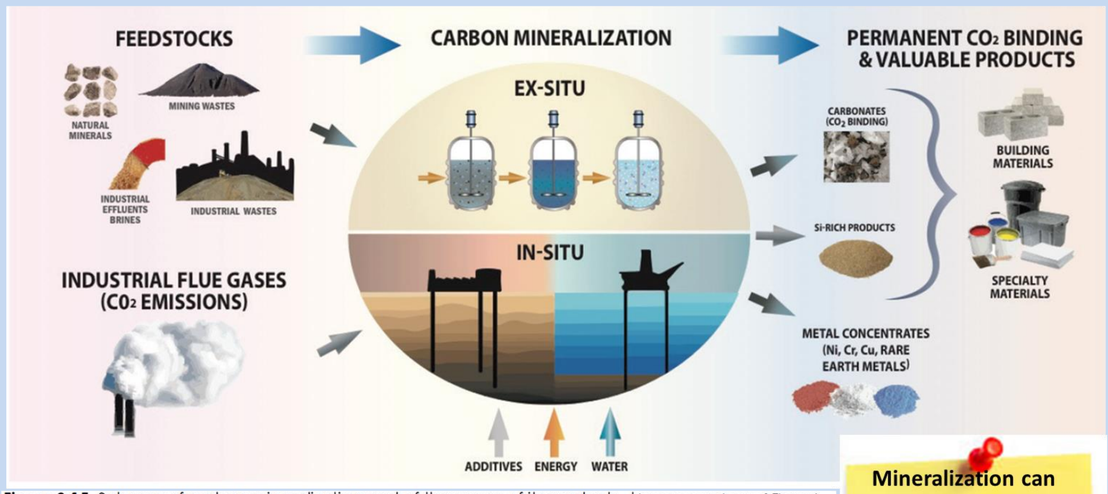
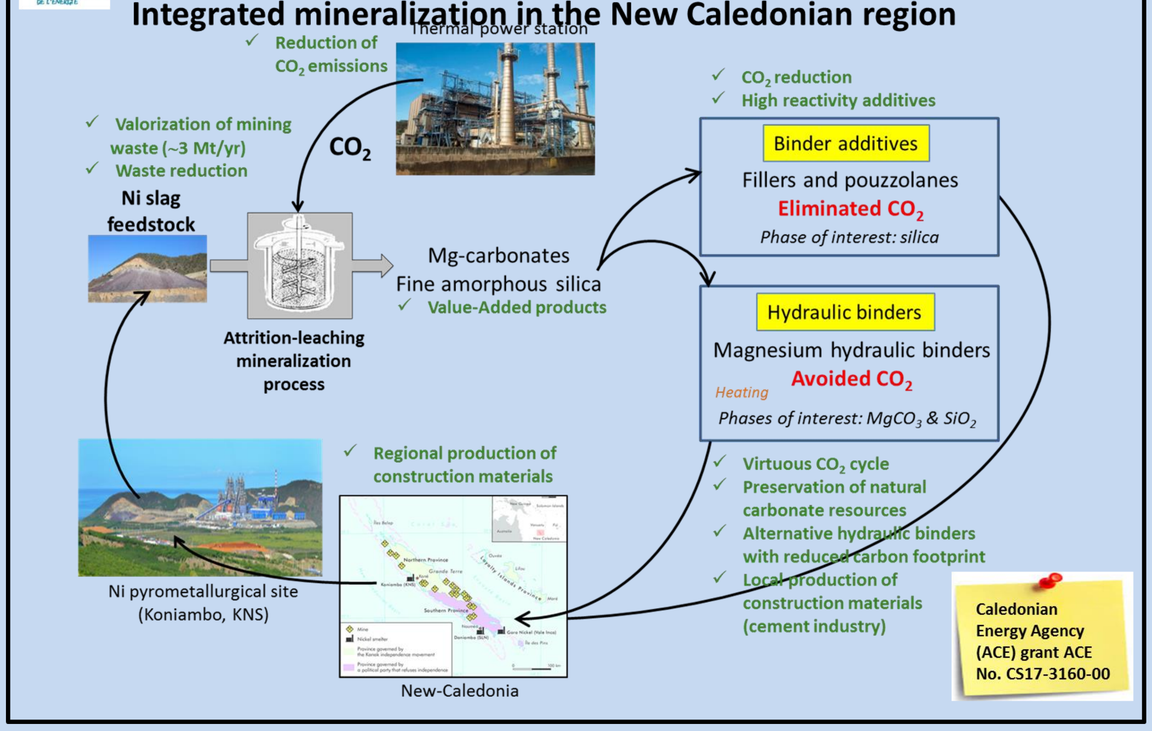


Figure 3.15. Scheme of carbon mineralization and of the range of its products. | Image courtesy of Florent Bourgeois, Laboratoire de Génie Chimique; Au-Hung Park and Xiaozhou Sean Zhou, Columbia University

Source: Mission Innovation Report , 2018[2]

Mineralization can meet the 3 criteria set by the IEA [1]:
- ✓ CO_2 emissions reduction
- ✓ Economic self-sufficiency
- ✓ Scalability

Integrated mineralization in the New Caledonian region



Geochemical modelling

Geochemical modelling an indispensable tool for development of mineralization processes

The challenge

Mineralization is a global niche market CO_2 mitigation solution. Its scope is territory dependent and combines feedstock selection, mineralization technology and product valorization through local materials supply chains. Development of mineralization pathways must integrate economic, environmental and technological assessment.

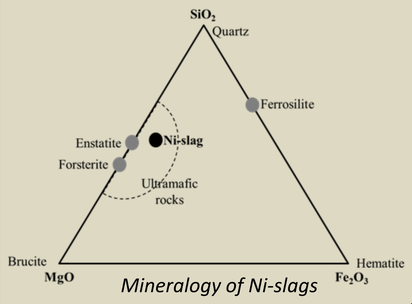
The proposed approach

Mineralization process metamodels are needed to provide input process data to a higher-level decision-making frameworks such as Life Cycle Analysis.

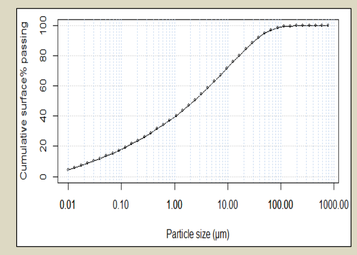
Geochemical modelling is a pivotal brick for mineralization modelling. Geochemical modelling is defined here as a modeling framework that predicts the evolution of the chemical composition of phases in the mineralization system, based on thermodynamic and kinetic models.

Application and geochemical model set-up

- Attrition-leaching mineralization process [1]
- Geochemical model inputs for feedstock of interest: Ni-slags



Mineralogy of Ni-slags



Particle size distribution

Geochemical modelling framework

- **Software: PhreeqC** [5]
- **Thermoddem version 2017 database**
- **R interface to PhreeqC** [6,7]

$$r = k_0 e^{\left(\frac{-E_a}{RT}\right)} a_{(H^+)}^{0.25} a_{(Mg^{2+})}^{-0.125}$$

Surface leaching rate model [8]

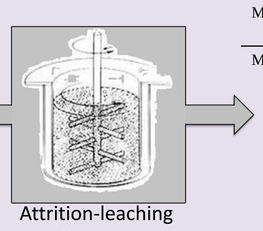
Results

Geochemical modelling : a guiding tool for mineralization feedstock & product valorization assessment

First-hand prediction of mineralization system speciation



Ni-slag ~ enstatite ($MgSiO_3$)
SiO2;MgO 0.824;
Fe_2O_3 0.104;Al_2O_3 0.022

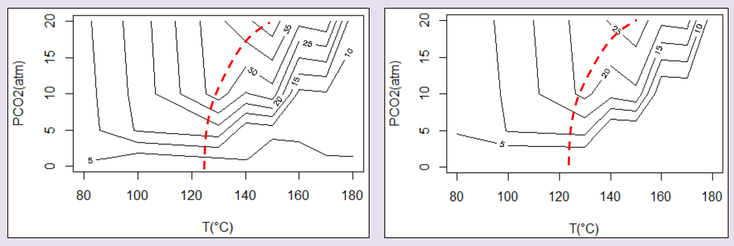


Attrition-leaching mineralization reactor

Desirable products

Phase type	Phase name	Formula
Carbonates	Magnesite (Synthetic)*	$MgCO_3$
	Siderite*	$FeCO_3$
Metal (hydr)oxides	Amorphous Silica	SiO_2
	Goethite	FeO(OH)
Magnesium silicates	Talc	$Mg_3Si_4O_{10}(OH)_2$
	Antigorite	$Mg_{48}Si_{34}O_{85}(OH)_2$
	Montmorillonite(HcMg)	$Mg_{0.3}Mg_{0.6}Al_{1.4}Si_4O_{10}(OH)_2$
	Sudoite	$Mg_2Al_4Si_3O_{10}(OH)_8$
	Chlinochlore	$Mg_5Al(AlSi_3)O_{10}(OH)_8$
	Beidellite(Mg)	$Mg_{0.17}Al_{2.34}Si_{3.66}O_{10}(OH)_2$
	Saponite(Mg)	$Mg_{3.17}Al_{0.34}Si_{3.66}O_{10}(OH)_2$
	Saponite(FeMg)	$Mg_{.217}FeAl_{0.34}Si_{3.66}O_{10}(OH)_2$
Other silicates	Minnesotaite	$Fe_3Si_4O_{10}(OH)_2$
	Chamosite.Daphnite	$Fe_5Al(AlSi_3)O_{10}(OH)_8$
	Pyrophyllite	$Al_2Si_4O_{10}(OH)_2$

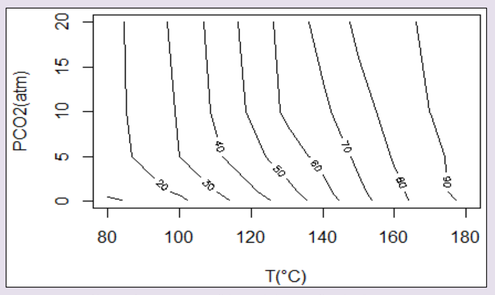
- **Attrition-leaching mineralization process**
- **Water + Ni-slag**
- **T = [100-180°C]**
- **P_{CO2} = [0.1-20 atm.]**



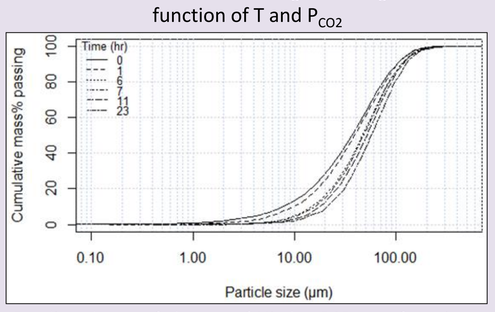
Predicted mass percent of carbonates (left) and amorphous silica (right) in mineralization product. Dotted lines indicate the best [T;P_{CO2}] set points.

Geochemical modelling : a guiding tool for mineralization process design

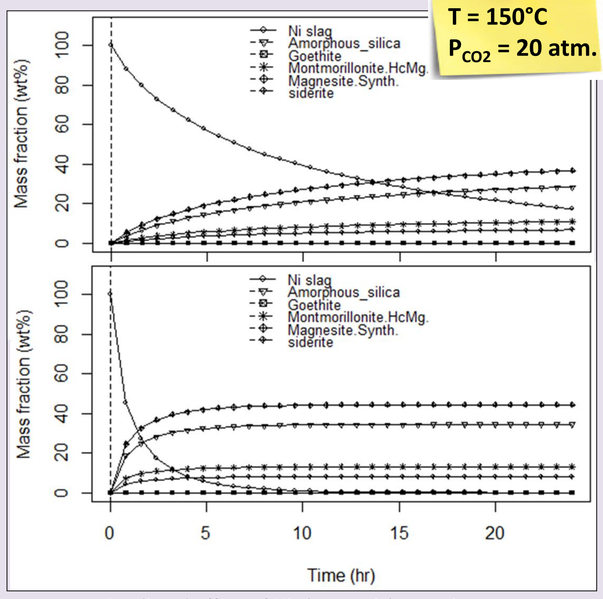
T = 150°C
P_{CO2} = 20 atm.



Predicted extent of leaching of Ni-slags as a function of T and P_{CO2}



Predicted rate of change of Ni-slag PSD as a function of attrition-leaching processing time



Predicted effect of Ni-slag particle top size on product speciation as a function of process time
Top figure: 100 µm; Bottom figure: 10 µm

Conclusions

- Mineralization is a promising CO_2 utilization solution that can meet all three criteria set by the IEA: CO_2 emissions reduction, economic self-sufficiency and scalability.
- Mineralization process development is challenging as its scope is territory dependent and combines feedstock selection, mineralization technology and valorization of mineralization products through local materials supply chains.
- The challenge with developing mineralization processes starts with the complexity and variety of mineralization systems' geochemistry.
- It is claimed that geochemical modelling is a pivotal building block for developing and modelling any mineralization process.
- Application to the attrition-leaching mineralization process for valorization of Ni-slags is used to exemplify the capacity of geochemical modelling as a mineralization process development guide. It is ideally suited for the attrition-leaching mineralization process as this process is unimpeded by surface leached layers and hence operates at the thermodynamic and kinetic limits of the feedstock.
- Geochemical modelling provides first-hand information critical to evaluation of both feedstock and product valorization potential. From an technological standpoint, geochemical modelling also provides insightful information about the effect of many operating variables on process performance.

Perspectives

- To harvest its full potential for mineralization process design, geochemical modelling must be embedded into a supervisory framework that converts geochemical model predictions into environmental and economic units, using regionalized impact and value assessment methods.
- The authors see significant potential in integrating geochemical modelling using PhreeqC into an LCA programming environment such as openLCA [9].
- A word of caution. If the potential of geochemical modelling for mineralization process design is indisputable, its depends strongly on user's expertise and critical thinking. It is no substitute for dedicated experiments, which are indispensable for fine tuning geochemical model settings. In the context of mineralization of Ni-slags by attrition-leaching, additional product characterization is underway to confirm the predicted speciation, with respect to Al content in particular, and coupling geochemical modelling with a validated attrition model is required for further process development and optimization.

References

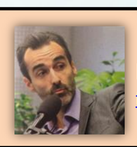
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SCIENCE AT THE CORE OF INDUSTRIAL PROCESSES