# INTEGRATION OF HYDROMETALLURGY PROCESS AND MINERAL CARBONATION TECHNOLOGY

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## ABSTRACT

The metal smelting and refining field is facing a dilemma to satisfy the social demand to reduce carbon dioxide  $(CO_2)$  emissions while maintaining supply chains by fulfilling the increasing demand for metal resources, such as for batteries and magnetics, as high-grade mineral resources continue to become depleted. Regardless of the market requirements, the need to respond to such social demands cannot be ignored.

Carbon dioxide capture, usage and storage (CCUS) is one of the measures to reduce  $CO_2$  emissions, and JGC has been developing its own technology by focusing on a CCUS using mineral carbonation ( $CO_2$  mineralization).

 $CO_2$  mineralization is a technology that reacts with and solidifies  $CO_2$  by forming chemical compounds with calcium and magnesium (Ca and Mg) sources such as basic rocks. As to the methodology of the reaction, a high-pressure method is commonly known, but JGC has been focusing instead on a method at atmospheric pressure.

In the beginning, a  $CO_2$  mineralization method using activated serpentine had been studied, however, a simplified economic study showed a negative result in terms of profitability due to its limited income based on carbon credits and magnesium carbonate sales revenue alone.

Conversely, in the field of nickel hydrometallurgy, acid leaching processes, such as high-pressure acid leach (HPAL), are attracting attention in recent years because the process produces nickel sulphate and mixed hydroxide precipitate (MHP) as the precursor materials of lithium-ion batteries (LiB) from nickel laterite ores. However, high-Mg ores have no affinity to the acid leaching process, as its Mg consumes the acid reagent and lowers the feasibility, therefore, high-Mg ores have not been actively processed but probably stockpiled at mine sites. JGC has developed a method to integrate the acid leaching process and CO<sub>2</sub> mineralization, which converts high-Mg ore into a nickel resource and reduces CO<sub>2</sub> emissions at the same time.

This paper introduces the abovementioned JGC's methodology and results of laboratory tests using actual nickel laterite ore samples and describes the improvement in a simplified economic study.

Keywords: carbon dioxide mineralization, sequestration, mineral carbonation, acid leach, nickel laterite ore

#### INTRODUCTION

 $CO_2$  mineralization technology is a technology that fixes  $CO_2$  as carbonate by reacting with calcium and magnesium, and sources of calcium and magnesium can be obtained from waste concrete, steel slag, coal ash, seawater, etc. While the most promising source is said to be basic rocks such as serpentine and olivine.

Conventionally, a method of activating serpentine by calcining, capturing  $CO_2$  through sequestration, and crystallizing for storage had been proposed <sup>(1)</sup>.

Crystallization:

 $5Mg^{2+}$  (aq) +  $4HCO_{3-}$  (aq) + $6OH^{-}$  (aq)  $\Box Mg_4(CO_3)_4$  (Mg(OH)<sub>2</sub>)  $4H_2O$  (s)

JGC investigated  $CO_2$  mineralization by applying waste concrete, seawater, and basic rocks (serpentine and olivine) as sources of the calcium and magnesium and dissolving the calcium and magnesium from these sources by varying the reacting conditions from pressurized to atmospheric and from high temperature to ambient and established a method to sequestrate  $CO_2$ . Particularly, a method to mineralize  $CO_2$  by dissolving Mg in basic rocks at atmospheric and ambient condition was established. Although the amount of magnesium extracted is small due to the lower partial pressure of  $CO_2$  compared to the high-pressure method, it can be positioned as a method that is easy to conduct because the equipment cost is lower, and operation and maintenance are easier than high-pressure/high-temperature methods. Moreover, an improvement of magnesium dissolution was achieved by grinding the magnesium source in the reactor system continuously to renew the residual surface and to reveal the activated part of the magnesium source. The laboratory test result showed the improvement in the amount of magnesium dissolved, that is, the concentration of magnesium in the liquid, by approximately six times.



#### Figure 1: Improvement of Mg dissolution by grinding in the reactor system

Based on the laboratory test results using serpentine, the amounts of  $CO_2$  mineralized and emitted were estimated. In this estimation,  $CO_2$  emission was derived from energy consumption by assuming Natural Gas (NG) fuels and NG power generation. As shown in Figure 2 it was confirmed that the amount of  $CO_2$  fixed for storage is expected to exceed the amount of  $CO_2$  emission.



Figure 2: Balance of CO<sub>2</sub> fixation and emission based on lab tests using serpentine

Further to the above, the income from carbon credits was calculated from the net  $CO_2$  fixation amount ( $CO_2$  fixation amount -  $CO_2$  emissions) and the unit price of carbon credits (assumed to be 150 USD/ton- $CO_2$ ) and compared with the operating costs calculated from the consumptions of heat and electrical power in the process. The unit prices of the heat and electrical power were assumed to be 3 USD/GJ and 0.1 USD/kWh, respectively. As shown in Figure 3, it was found that  $CO_2$  mineralization using serpentine would not be feasible in terms of profitability.



### Figure 3: Income from carbon credit vs expenses for energies consumed in the process

JGC's idea to improve the economic feasibility of  $CO_2$  mineralization is to integrate  $CO_2$  mineralization technology with metallurgical processes. In addition to the fundamental benefits of not only reducing  $CO_2$  emitted from the metallurgical processes, but also revenue from metal products and cost savings by sharing common facilities such as infrastructures and utilities, there are additional opportunities to convert low grade difficult-to-processing ores that are untapped and stockpiled at mine sites to processable ores, especially when looking at nickel acid leaching as a hydrometallurgical process. This is to say, in the acid leaching process, high-Mg ores are left untouched because the magnesium in the ore consumes the leaching agent

sulfuric acid, whereas carbonation processing removes the magnesium from the ore and as a result expands the amount of nickel resources that can be processed in an economically feasible way. A schematic block flow diagram of the integration process is shown in Figure 4.



Figure 4: Integration of CO<sub>2</sub> mineralization and Ni acid leaching processes

Figure 5 shows a profile of a typical laterite deposit. Normally, an acid leaching process treats laterite mainly existing in the surface layer, and the nickel grade is at most about 1 wt%, but profitability is ensured because there is less magnesium, which consumes the leaching agent sulfuric acid. High-Mg ores have generally been processed using a pyrometallurgy/smelting method, which consumes a lot of energy, but the high nickel grade makes it profitable.

SCHEMATIC LATERITE PROFILE		APPROXIMATE ANALYSIS (%)		EXTRACTION			
		Ni	Co	Fe	MgO	PROCESS	
	RED LIMONITE	<0.8	<0.1	>50	<0.5		CID
	YELLOW LIMONITE	0.8 to 1.5	0.1 to 0.2	40 to 50	0.5 to 5	CARON	
	TRANSITION	1.5 to 4		25 to 40	5 to 15		SMELTING
	SAPROLITE/ GARNIERITE/ SERPENTINE	1.8 to 3	to 0.1	10 to 25	15 to 35		
	FRESH ROCK	0.3	0.01	5	35 to 45		

Figure 5: Schematic Laterite Profile (Elias 2002)

Assuming that a laterite ore with a nickel content of 1 wt% and a magnesium content of 20 wt% is used as a feedstock for an acid leaching process (HPAL, etc.), the cost impact of reducing magnesium in the ore and reducing  $CO_2$  through  $CO_2$  mineralization was estimated.

The magnesium in the ore consumes sulfuric acid in the leaching reactor, and at the downstream neutralization process with limestone it generates another  $CO_2$ .

 $\begin{array}{rcl} MgO(s) + H_2SO_4(aq) & \Box & MgSO_4(aq) + H_2O \\ MgSO_4(aq) + CaCO_3(s) & \Box & MgO(s) + CaSO_4(s) + CO_2(g) \end{array}$ 

The amount of  $CO_2$  generated when ore containing 20 wt% of magnesium is processed in an acid leaching plant was estimated, and the carbon credit for reducing magnesium in the ore through  $CO_2$  mineralization treatment was calculated based on the amount of magnesium in the residue after mineralization. In addition, the amount of sulfuric acid consumed by the acid leaching plant from magnesium remaining in the residue without being extracted during the  $CO_2$  mineralization process was estimated and compared it in a graph along with carbon credits.

In this study, the carbon credit was assumed to be 150 US/t-CO<sub>2</sub> and the sulfuric acid cost was 150 US/t-Acid (see the estimation conditions in Table 1 below).

Mg content in the ore Free acid at the outlet of acid leaching Carbon credit	20 wt% 50 g/L 150 US\$/t-CO <sub>2</sub> 150 US\$/t-Acid
Sulfuric acid cost	150 US\$/t-Acid



Figure 6: Economical study for carbon credit and acid consumption by magnesium

When ore feedstock containing 20 wt% of magnesium is processed as is in the acid leaching plant without mineralization, the sulfuric acid consumed by the magnesium in the ore is approximately equivalent to 115 US\$/ton-Ore. Reducing magnesium in the ore through  $CO_2$  mineralization reduces sulfuric acid consumption in the acid leaching plant and increases carbon credits simultaneously. Reducing the residual magnesium in the ore after  $CO_2$  mineralization to 8 wt% offsets the cost of sulfuric acid consumed by residual magnesium and the carbon credits. If the residual magnesium in the ore after  $CO_2$  mineralization treatment is further reduced, the economic efficiency of  $CO_2$  mineralization becomes superior.

## **EXPERIMENTAL APPARATUS / TEST CONDITIONS**

High-Mg nickel laterite ores were collected from various areas and subjected to laboratory tests. In this laboratory test, calcined ore, water, and alumina balls were placed in a separable flask with a capacity of 2000 ml, and  $CO_2$  was supplied while stirring with an agitator to dissolve magnesium. A photo of the equipment used in the laboratory test and a photo of the ore sample used in the test are shown in Figure 7, and the composition of the ore is shown in Table 2.



Figure 7: Experimental apparatus (left) and ore sample (right)

Composition	[wt%]		
Ni	0.90		
Fe	6.82		
Со	0.02		
Mg	22.4		
Si	19.7		
С	1.66		
S	0.01		
Al	0.08		
Са	0.01		

# Table 2: Composition of ore sample

The test procedure is summarized in below Table 3.

#### Table 3: Test Procedure

Comminution	The ore sample was crushed to obtain particles under 150 $\mu$ m.
Calcination	Calcine the ore at 500 – 700° C for 30 minutes using muffle furnace.
Magnesium dissolution	Calcined ore, water, and alumina balls were put in the flask, and $CO_2$ gas was supplied while stirring with the agitator to dissolve magnesium.
Crystallization	After magnesium dissolvement, residues were removed from Mg dissolved solution. Then crystallize magnesium carbonate by air bleeding to the solution.

In the magnesium dissolving process, JGC's unique method (patent pending) to grind the ores in the reactor system was simulated by stirring the ore slurry together with alumina balls, that is, allowing the reaction to

occur while renewing the residual surface and exposing the activated part of the calcined ore through abrasion.

In the past laboratory test result using serpentine showed the improvement in the amount of magnesium dissolved, that is, the concentration of magnesium in the liquid, by approximately six times. (See Figure 1)

## **TEST RESULTS**

## Calcination

The image of weight loss observed in the results of TG (Thermogravimetry) for laterite ore is shown in Figure 8. Similar to serpentine, a significant weight loss was observed above 500° C, which is considered to be due to the removal of crystal water in the ore. Based on the TG results, the calcining temperature was set at 500-700° C.



Figure 8: TG trend in ore sample calcination

### Magnesium dissolution

One of the results of changes in magnesium concentration in the liquid during the magnesium dissolution tests is shown in Figure 9. Although the final magnesium concentration differed depending on the test conditions, there was a tendency for the magnesium concentration to reach a plateau in about 2 hours under most conditions. Furthermore, it has been confirmed that nickel loss from the ore into the magnesium carbonate solution was negligible.



Figure 9: Magnesium concentration in the dissolution test

# Crystallization

A photograph and SEM (Scanning Electron Microscope) image of magnesium carbonate obtained from the crystallization test are shown in Figure 10. White crystals with a needle-like structure were obtained.



Figure 10: Photo (left) and SEM image (right) of magnesium carbonate obtained from crystallization

The results of XRD analysis for the obtained crystallized carbonate are shown in Figure 11. The XRD results showed that there were no sharp peaks, and it was difficult to identify the crystallized substances by XRD. Nesquehonite (MgCO<sub>3</sub> ·3H<sub>2</sub>O), Hydromagnesite (Mg<sub>5</sub>(CO<sub>3</sub>)<sub>4</sub>(OH)<sub>2</sub> ·4H<sub>2</sub>O) and Dypingite (Mg<sub>5</sub>(CO<sub>3</sub>)<sub>4</sub>(OH)<sub>2</sub> ·5H<sub>2</sub>O) are known as Mg-CO<sub>2</sub>-H<sub>2</sub>O type magnesium carbonate<sup>(2)</sup>. It has also been reported that amorphous magnesium carbonate is produced as a precursor of magnesium carbonate hydrate<sup>(2)</sup>.

To identify the crystallized material, TG analysis of the crystallized material was performed, and the results are shown in Figure 12. Since it matches well with the TG trend of the reagent Hydromagnesite, the crystallized product is considered to be Hydromagnesite.



Figure 11: XRD analysis of crystallized material



Figure 12: TG analysis of crystallized material

# Transition of ores/residues structures through calcination to magnesium dissolution

Figure 13 shows SEM images of the ore samples, calcined ores and residues after magnesium dissolution for the past serpentine test and laterite ore test. Corresponding specific surface areas are shown in Table 4, where measurement of the surface areas SA are shown in the left column and calculations based on the

equation (1) – a calculation of the surface areas  $S\omega$  based on the particle size distributions by assuming all the particles being spherical bodies - are shown in the right column.

$$\mathbb{X}_{\mathbb{N}} \boxtimes \frac{\mathbb{X}}{\mathbb{N}} \frac{\mathbb{X} \boxtimes \boldsymbol{n}_{\mathbb{N}} \mathbb{X}}{\mathbb{X} \boxtimes \boldsymbol{n}_{\mathbb{N}} \mathbb{X}}$$
(1)

ρ: density



#### Figure 13: SEM Images of ore samples, calcined ores and residues

	Measured Surface Area: SA(m <sup>2</sup> /g)		Calculated Surface Area: $S_{\omega}(m^2/g)$		
	Serpentine	Laterite Ore	Serpentine	Laterite Ore	
Raw Ore	17	127	1.58	0.03	
Calcined	34	110	1.44	0.31	
Residue	81	234	0.97	1.27	

#### Table 4: Surface Areas of ore samples, calcined ores and residues

From the SEM images and specific surface areas, it was found that the surfaces of all these solid contents were porous, and the surface areas increased due to the process through calcination and magnesium dissolution reaction. It can be assumed that through calcining and Mg dissolution process, the surface of the ores would become porous as hydroxides and magnesium compounds being removed from the structures.

The SA and S $\omega$  of the serpentine represent such a phenomenon (SA increased by five times while S $\omega$  maintained and even reduced a bit).

When comparing the serpentine and the laterite ore, it is presumed that the laterite ore (raw ore, calcined

and residues) were more porous, but increase in SA through the process was relatively low while S $\omega$  increased considerably. This is to say, laterite ore may remain with a potential to increase in porousness, i.e., to increase activated parts.

#### **ECONOMIC STUDY**

### Study conditions/assumptions

Based on the laboratory test results of  $CO_2$  mineralization using nickel laterite ore with a magnesium content of 22 wt% and assumptions derived from the laboratory test results, the amount of  $CO_2$  fixed in the mineralization process and the power and heat consumptions to operate the facility were estimated. The energy and heat consumptions were converted into  $CO_2$  emissions using the specific  $CO_2$  emissions

intensity for LNG fuels and LNG power generations. Table 5 below summarizes the estimation conditions for the study.

Mg content in the ore	22 wt%
Moisture content in the ore	20 wt%
Rate of mineralized CO <sub>2</sub>	83 %
Mg utilization (dissolution) rate	41 %
CO <sub>2</sub> emissions intensity	
Electrical power	0.4 kg-CO <sub>2</sub> /kWh (NG power)
Heat	50 kg-CO <sub>2</sub> /GJ (NG fuel)

#### Table 5: Conditions/assumptions for economical study

### **Study result**

Comparing the amount of  $CO_2$  fixed in the mineralization process and the equivalent amount of  $CO_2$  emissions required to operate the mineralization facility shown in Figure 14 below, the amount of  $CO_2$  fixed well exceeds the amount of  $CO_2$  emissions.

Most of  $CO_2$  emissions come from energy sources such as calcining heat (including free water drying) and crystallization energy, and it is possible that a large part of them can be reduced by using green electricity and green fuel.



### Figure 14: Comparison of CO<sub>2</sub> fixed vs emitted as energies consumed in the mineralization process

The test results using the actual laterite ores showed above explains that the utilization (dissolution) rate of magnesium in the mineralization process is not high, and the magnesium remaining in the residue consumes sulfuric acid in the acid leaching process and generates  $CO_2$  in the neutralization process. This has not resulted in a significant reduction in  $CO_2$  emissions.

If high-Mg ores can be converted to ores processable in the acid leaching method, it is expected that the range of ore resources will expand and production of nickel and cobalt will increase, and the profitability of  $CO_2$  mineralization will be improved.

Furthermore, by optimizing the magnesium concentration in the feedstock of nickel acid leaching process and the operating conditions of the mineralization process in accordance with the properties of the nickel laterite ores, e.g., magnesium contents, it is expected to improve the magnesium dissolution rate and reduce the energy consumption.

## DISCUSSION

According to the test results and economic study results, although the effect of removing magnesium from the high-Mg ore was observed similarly with serpentine, the current level of magnesium utilization (dissolution) is only about 40%, whereas the magnesium remaining in the residue will consume the leaching agent in the acid leaching process and generate another  $CO_2$  emission in the neutralization process at the downstream.

Therefore, it is necessary to reduce the magnesium in the residue before feeding to acid leaching process as much as possible. As a guideline, when  $CO_2$  mineralization is applied to 20 wt%-Mg ore, if the magnesium remaining in the residue could be reduced to about 8 wt%, that is, the amount of magnesium dissolved can be increased to about 60%, the integration process of  $CO_2$  mineralization and acid leaching technology reduces overall  $CO_2$  emission.

Figure 15 shows a simple calculation of the overall  $CO_2$  emissions when blending the residue from  $CO_2$  mineralization of 20 wt%-Mg ore with Mg-free nickel laterite ore. As discussed above, the magnesium utilization (dissolution) rate directly dominates the effectiveness of  $CO_2$  emission or reduction, and the effectiveness in whichever emission or reduction is eased off by ore blending with  $CO_2$  mineralization residue.

It is also necessary to consider reducing the energy required for mineralization, including the calcination process, and supplying the energies from sources other than fossil fuels.



Figure 15: Effect of Mg reduction from high-Mg ores in CO<sub>2</sub> mineralization process

### Ideas to improve magnesium dissolution

#### Ore particle size

It would be possible that the reactivity can be improved by pulverizing the high-Mg ore more finely and exposing the surfaces to be activated. However, it is necessary to keep it within a range that does not affect sedimentation.

#### Activation of magnesium in ore

It would be possible to improve the ore activation by extending the calcining time or by applying internal heating method by using microwaves or the like to ensure even calcining and to prevent inactivated portions from remaining.

Since it has been reported possible to modify serpentine into highly active olivine <sup>(3)(4)</sup>, the application of microwave calcining technology seems promising.

### Adjustment of dissolution temperature

Figure 16 shows Magnesite Saturation Indexes  $^{(5)}$  a measure of degree of supersaturation, defined as the base 10 logarithm of the ion activity product divided by the solubility product constant. Although the solubility of carbon dioxide becomes lower at higher temperatures, the solubility of Mg-CO<sub>2</sub>-H<sub>2</sub>O type magnesium

carbonate increases even at higher temperatures, and there would be a sweet spot to optimize the magnesium dissolution by adjusting the dissolving temperature.



Figure 16: Summary of literature data versus simulated magnesite saturation indexes <sup>(5)</sup>

#### Ideas to improve energy consumption

#### Alternative energies

Although LNG is assumed as the power and heat sources in the study, it is possible to reduce CO2 emissions by applying green fuels (hydrogen, ammonia fuel), and green electricity. The microwave mentioned above is also an alternative method that uses electricity, so it is expected that both problems can be solved at the same time.

### CONCLUSION

A reaction similar to the CO<sub>2</sub> mineralization reaction observed in serpentine was confirmed in lab tests using nickel laterite ores by JGC's method at atmospheric pressure.

It was suggested that the integration of  $CO_2$  mineralization and nickel acid leaching process could satisfy both the reduction of  $CO_2$  emissions and profitability.

Future challenges include optimizing the amount (concentration) of magnesium dissolution by adjusting conditions and methodologies in comminution and calcining process.

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