NIPPON STEEL & SUMITOMO METAL TECHNICAL REPORT No. 109 JULY 2015

Technical Report

UDC 669 . 184 . 28 : 639 . 25

Development of a Continuous Rapid Carbonation Process for Steelmaking Slag

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Abstract

After fundamental laboratory studies on expanding the utilization of steelmaking slag, envisaging especially its marine applications, a pilot plant for rapid slag carbonation was built at Nagoya Works in 2004. The plant was mainly intended for supplying carbonated slag for tests in the sea on the problem of white turbidity of seawater due to the elution of alkaline components from slag. After initial equipment troubles and measures to solve them, the plant was brought into stable operation, and the operating conditions for continuous processing have been defined. A total of 1800 tons of steelmaking slag has been processed through the plant since 2005, and used for the tests, some under governmental auspices, of sand covering, mound forming, algae bed revitalization, etc. at sea bottoms. As a result, the marine use of carbonated steelmaking slag has proved viable.

1. Introduction

To expand effective utilization of steelmaking slag, especially for marine applications, in 2002, Nippon Steel & Sumitomo Metal Corporation commenced studies to develop a slag reforming process by carbonation as a measure to prevent alkali elution from slag, which caused the white turbidity of seawater. The study subjects included the basic mechanisms of carbonation reaction, the factors influencing the rate of carbonation when a laboratory-scale facilities were scaled up,[1] etc. The studies have led to the quantification of the conditions under which the carbonation of slag progresses far more rapidly than that by the formerly reported method of forming carbonated blocks [2] at room temperature.[3]

In the meantime, the Ministry of Economy, Trade and Industry commenced discussions on a project named "the technical development for the marine use of steelmaking slag" in the autumn of 2003. In the discussions, the rapid slag carbonation process was considered to be effective to solve the most serious problem in the marine use of steelmaking slag, the white turbidity, and thus give the project the impetus to go forward. Accordingly, it was decided that based on its own technology, Nippon Steel & Sumitomo Metal would build a test plant capable of supplying meaningful amounts of carbonated slag.

The test plant was built at Nagoya Works of the Company in October 2004, and various test runs and corrective measures aiming at stable and continuous operation to eventually attain stable operation were conducted. The present paper reports the outlines of the plant, the result of the trial production of carbonated slag at the design capacity from the summer 2005, and the results of different kinds of trial applications of the carbonated slag in the sea.

2. Outlines of the Test Plant for Slag Carbonation Using Rotary Mixer

The location of the test plant was discussed from the perspective of it being the supply base of carbonized slag for the verification tests in sea as an important part of the project under Government funding. Nagoya Works was finally chosen because a series of precedent tests of carbonating steelmaking slag in batches of several tons each (all the units herein are metric) had been conducted there using the drums of concrete mixer trucks.

To make the most of the findings obtained through the precedent tests and to confirm the productivity, plant capacity, and processing costs for future commercial production in quantities, a horizontal

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rotary mixer was selected as the vessel for the continuous carbonating process. Accordingly, a rotary mixer, 1 m in inner diameter and 12 m in length, that was originally used for drying sea sand (see **Photo 1**) was brought in to the Works in March 2004, and installed at the designated area in October of the same year. **Figure 1** is an elevation view of the pilot plant, **Table 1** shows its specifications, and **Photos 2** and **3** show the inlet and outlet ends, respectively, of the mixer after installation.

3. Problems Related to Carbonation Behavior during Test Runs and Corrective Measures

After cold runs to confirm the soundness of the equipment and tune the electrical systems, test carbonation of steelmaking slag commenced in November. **Table 2** shows the main processing conditions, and **Table 3** depicts the actual operation parameters measured during the trail runs.

Steelmaking slag is heavier than the sea sand for which the mixer was originally designed, and hence, problems surfaced when the slag was charged into the mixer: the shafts of the mixer support rollers and the roller bearings at the outlet end to prevent the mixer from dislocating broke under the load. Test runs were conducted in a batch processing regime, i.e., intermittently charging the material slag, while measures to solve different problems were taken. As a result, it was found that the free CaO (f-CaO) in the slag was lowered to around 1% through roughly 2 h of processing, as had been confirmed through laboratory tests [1] (see **Fig. 2**). Based on this result, 1 ton of carbonated slag (see **Photo 4**) was shipped in mid-December to the Fisheries Research Laboratories of the Fisheries Agency for safety evaluation before the trial use of the processed slag in marine environments for the project.

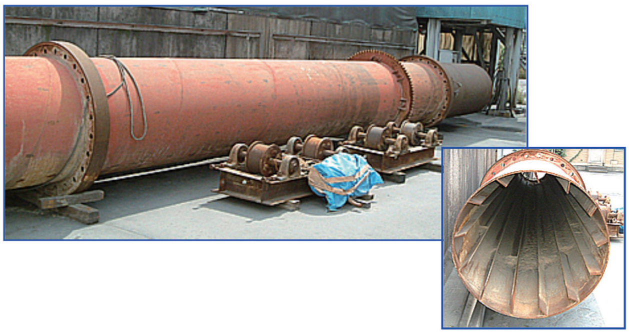

Photo 1 Rotary mixer for pilot plant

Table 1 Specifications of carbonation pilot plant

Component	Type classified	Specification	
Inlet conveyor	Climber type	1.0	t/h
Rotary mixer	1 m$\phi \times$12 mL	9–36	rpm
Reduction gears	Bayern type	84–336	rpm
Outlet conveyor	Climber type	1.0	t/h
Ventilator	Turbo blower #18	7.5	m^3/min
Total gas regulator	Flow type meter	420.0	m^3/h
CO_2 flow regulator	Flow type meter	24.8	m^3/h

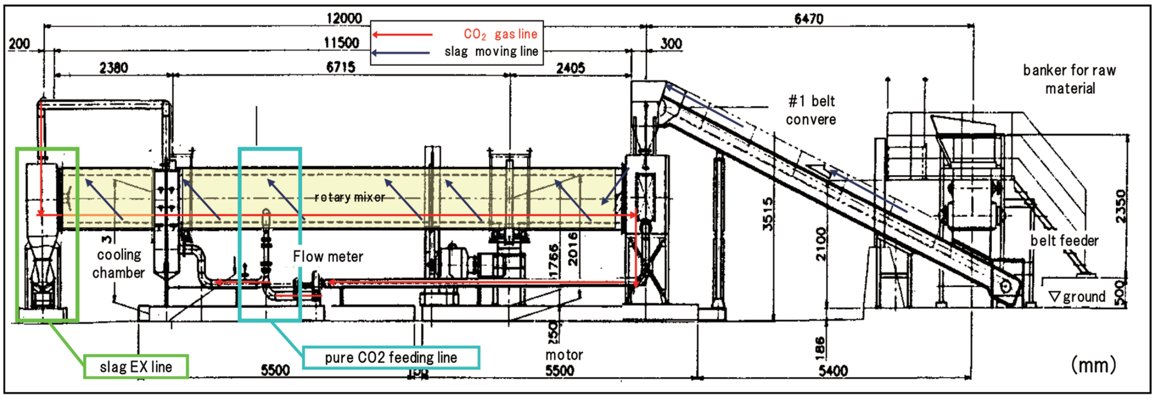

Fig. 1 Rotary mixer type continuous carbonation pilot plant

Photo 2 Mixer outlet section

Photo 3 Mixer inlet section

In addition to the equipment problems during the test runs, however, a serious quality problem occurred: the content of f-CaO in the treated slag was not maintained stably below 1%. The cause was speculated and countermeasures against them were discussed. Eventually, as a result of decreasing moisture addition to the feed slag, the carbonation reaction was sustained for more than 1 h, and the initial target, a f-CaO content less than 0.9%, was attained in March 2005 (see **Fig. 3**).

Table 2 Operation conditions for test runs

Rotational speed	10.0	rpm
Watering pressure	0.14	MPa
Water drain rate	0.9	l/min
Slag feeding rate	0.8	ton/h
Gas ventilation rate (see Table 3)		

Then, the test use of carbonated steelmaking slag for sand cover of sea bottom and mounds forming (tideland) in offshore of Sakai, Osaka (Sakai Bay I in Table 4), was officially included in the national budget for the fiscal year 2005. At that time, however, it was considered difficult to sustain continuous operation to supply the required amount of the product with temporary measures taken individually against different equipment problems, and a series of more fundamental and strengthening modifications were introduced. The modifications included the reinforcement of the thrust bearings to prevent the mixer from dislocating (see **Photo 5**).

4. Process Behavior of Continuous Slag Carbonation after Plant Modifications and Production for Shipment of Carbonated Slag

The above strengthening modifications were completed in July 2005, and immediately thereafter, various operation parameters were redefined for continuous production at the design capacity.

Table 3 Measurements at trial runs

	Measured % CO_2 in gas		Slag feeding rate	Gas blowing rate	CO_2 feeding rate	Estimated Δ CaO under ideal condition		
	Inlet	Outlet						
	(%)	(%)	(kg/h)	(Nm^3/h)	(Nm^3/h)	Initial	Δ CaO	Estimated
1st run	16.7	13.6	800	363	11.2	7.00%	0.90%	6.10%
2nd run	22.0	18.0	800	332	15.2	7.00%	1.30%	5.70%

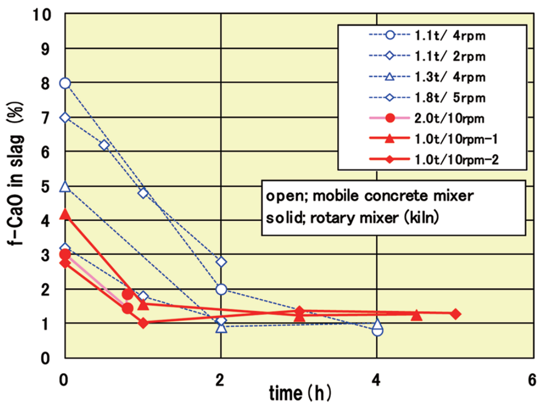

Fig. 2 Change in f-CaO in slag at trial runs

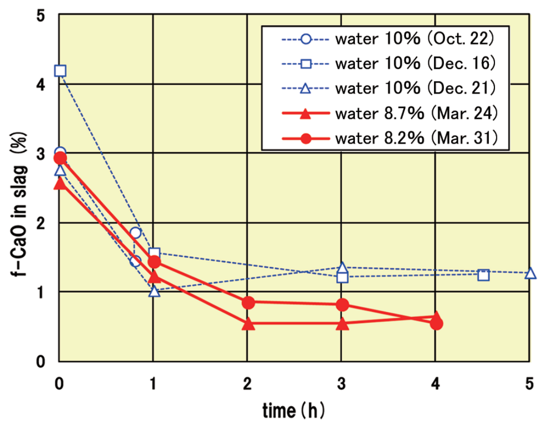

Fig. 3 Change in f-CaO in slag under different moisture contents

Photo 4 Carbonated steelmaking slag at the trial run

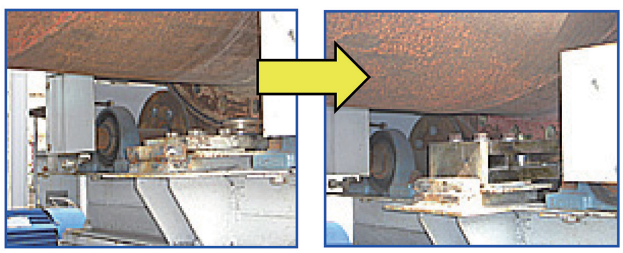

Photo 5 Thrust bearing modification

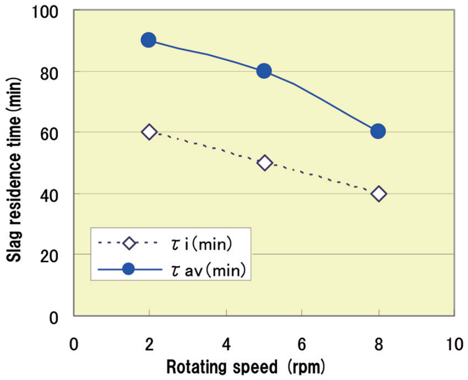

Fig. 4 Relationship between the rotation and slag residence time

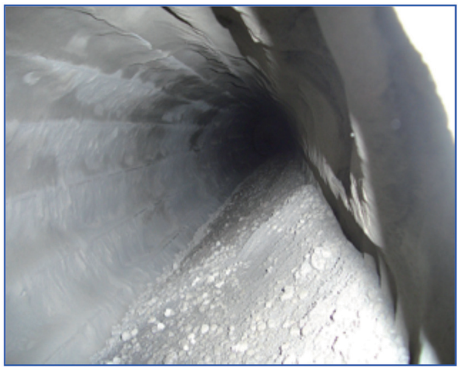

Photo 6 Slag behavior inside mixer (seen from inlet end)

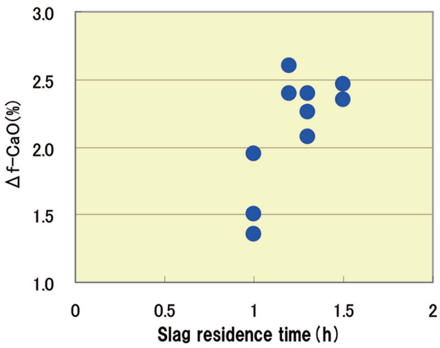

Fig. 5 Influence of slag residence time on the carbonation

Photo 7 Carbonated steelmaking slag for National Project

Figure 4 shows the result of the test to confirm the change in the resident time of slag in the mixer using colored slag and changing the mixer rotation. It became clear that an average resident time of approximately 90 min could be secured by decreasing the rotation rate, and consequently, the decrease in the f-CaO due to the carbonation per unit residence time could be increased, as shown in **Fig. 5**.

In addition, it was announced that the grain size of the slag used for the sand covering of the ministerial tests was changed from less than 25 mm, which had been the target product size of the plant, to less than 5 mm. On the other hand, when the slag contained a high percentage of fines, it had been found that the processing efficiency tended to fall even at high mixer filling factors, because only the surface layer portion of the slag bed in the mixer contacting the gas was renewed by the rotation.[4)] In consideration of this and the above size change, it was decided that continuous operation would proceed at a processing rate of around 2 tons/h and the filling rate would be controlled to about 15% or less, the same as in the past drying operation, and the filling and flowing conditions of the slag in the mixer would be monitored (see **Photo 6**).

Under the above conditions, continuous operation of slag carbonation began in August 2005. Up to the end of that year, 1000 tons of the product was produced in total and shipped to the test site (see **Photo 7**). In the first stage of the test offshore Sakai under the governmental funding from January 2006, the carbonated steelmaking slag was dumped into the sea without causing the white turbidity of seawater,[5)] which had been a long-standing problem in the marine use of slag. A second batch of roughly 850 tons of carbonated slag was produced and shipped to Sakai for the second stage of the test in the summer of 2006 (Sakai Bay II in Table 4).

5. Application of Developed Rapid Slag Carbonation Process from Other Works

The Company still had to confirm whether the developed carbonation process was applicable to the slags of the other works. To verify this, slags of Kimitsu and Muroran Works were sent to Nagoya, processed through either the rotary mixer or concrete mixer drums, and shipped to different organizations as samples for evaluation; see **Table 4** for more detail.

The developed slag carbonation method was confirmed to be capable of substantially producing the same product using slags from different works as the raw material. After that, about 200 tons of slag was carbonated at Muroran through a rotary mixer for use in mound formation or in artificial ferrous units for fostering algae beds (to be mentioned herein later). On the other hand, fine slag from secondary steel refining processes was carbonated at Kimitsu by the mixer truck method for test purposes. It was newly found through this test that it was possible to carbonate and simultaneously granulate fine slag by adequately controlling the addition amount of water.[6)]

6. Trial Uses of Carbonated Slag for Marine Applications

6.1 Sand covering and mound forming

Aiming at rationalizing energy use and improving marine environment, the activities for the government-funded project "R&D for the Effective use of Slag," mentioned in Section 4, started in 2004 to develop ways of harmlessly using steelmaking slag for marine applications. As part of the project, the rapid carbonated slag from Nagoya Works was used in quantities for the tests of sand covering

Table 4 Shipping list of carbonated slag from several works treated at Nagoya Works

Period	2004 July	2004 July	2004 August	2004 September	2004 December	2005 February	2005 Aug.-Dec.	2006 April-July
Shipped to:	Tokushima Univ. (Obayashi)	Mashike (Tokyo Univ.)	Tokai Univ.	Mashike Bay	Fisheries Research Agency (National Pj)	Toa Const.	Sakai Bay I (National Pj)	Sakai Bay II (National Pj)
Final application	Artificial beach	Ferrous unit	Artificial beach	Ferrous unit	Toxicity test	Bottom capping	Sand cover & mound	Sand cover & mound
Processing vessel	Concrete mixer	Concrete mixer	Concrete mixer	Concrete mixer	Rotary mixer (kiln)	Concrete mixer	Rotary mixer (kiln)	Rotary mixer (kiln)
Slag species	Nagoya ORP	Nagoya ORP	3 types of Kimitsu	Nagoya ORP & Muroran	Nagoya ORP	Kimitsu 2nd ref. slag	Nagoya ORP	Nagoya ORP
Size, amount	< 8 mm, 1 t	< 8 mm, 50 kg	< 5 mm, 300 kg each	< 25 mm, 20 t	< 25 mm, 1 t	< 8 mm, 1 t	< 5 mm, 850 t	0–25 mm, 850 t

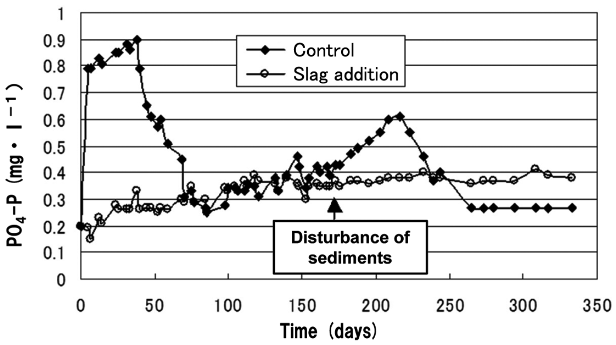

Fig. 6 PO_4-P concentration behavior with/without carbonation slag

and forming algae beds (mounds) offshore Sakai since 2005. At the follow-up monitoring, the phosphate concentration in the interstitial water at the test site was reported to be lower than that at a comparative area using natural sand bottom,[5] which indicated that the water had been purified.

On the other hand, as an advance evaluation for such large-scale test at the sea, Miki et al. had conducted laboratory tests of mixing carbonated slag with sea-bottom soil and confirmed that the PO_4-P concentration in the seawater in the zone where carbonated slag had been administered was maintained lower than that in the zone without it, and the rapid elution of PO_4-P was suppressed as shown in **Fig. 6**.[7]

6.2 Revitalization of algae beds

Besides the above, steelmaking slag treated through the rapid carbonation process was mixed with artificially fermented humus and formed into iron supply units to supply iron ions to seawater. Since autumn of 2004, in a trial to restore algae beds, these units were planted at the seabed along the Shaguma coast, Mashike Town, Hokkaido, where algae had run dry, and consequently, the population of underwater animals drastically decreased (called rocky-shore denudation or sea bottom desertification),[8, 9] and in the spring the following year, kelp was found to grow thickly. Through periodical observation every year thereafter, the algae beds have been found to be well revitalized since then.[10]

In consideration of the above, the method of revitalizing algae beds by supplying iron has been tested; as seen in **Fig. 7**, it is being tested in more than 30 waters all over Japan. Meanwhile, it has been reported that, in supplying iron (more specifically, divalent iron, or ferrous ions) to seawater, the saturation solubility of iron falls when the pH of the seawater is high,[11] which indicates that the slag carbonation process is key to differentiating the artificial ferrous units from other similar products.[12]

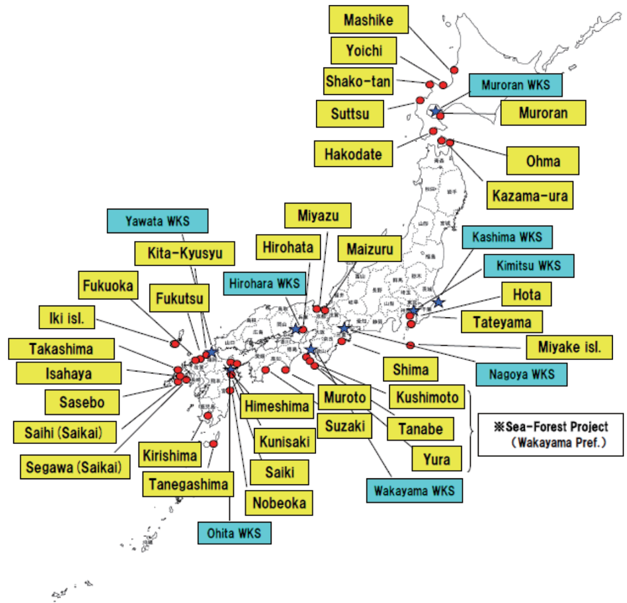

Fig. 7 Test sites of algae bed restoration using artificial ferrous units

Besides the tests of algae bed revitalization in Fig. 7, various laboratory tests have been conducted on the effects of the use of carbonated slag over algae; in fact, the effects of carbonated slag over laver (dried and used for wrapping sushi rolls, etc.)[13] and benthic microalgae[14] have come to be discussed in academic circles.

7. Conclusion

Aiming at expanding the utilization of steelmaking slag, especially for cultivating its new applications in the sea, elementary technologies for its rapid carbonation were developed through laboratory tests. To clarify the process behavior of the slag carbonation in an enlarged scale envisaging commercial production and to supply carbonated slag for tests in the sea, a pilot plant using a rotary mixer was constructed at Nagoya Works.

After the start-up in autumn 2004, countermeasures were taken against equipment problems and the conditions for stable operation were defined. Since the summer of 2005, roughly 1800 tons of steelmaking slag was carbonated and shipped for tests of sand covering, formation of tideland mounds (mostly under government funding), and revitalization of algae beds.

The slag carbonation process made it possible to suppress the white turbidity of seawater due to alkali elution from slag, and therefore, carbonated slag was used for reforming sea bottoms at the tests offshore Sakai as part of the "R&D for Effective Use of Steel Slag" under government auspices. The R&D yielded a new slag product called the CaO-improved soil, combining steelmaking slag with the dredged soil from sea bottoms and usable in quantities for filling sea-bottom depressions. A guide book[5] on the marine use of steelmaking slag was published to promote the application method.[15] As a result of the above, the use of carbonated slag became limited to the supply of iron ions for revitalizing algae beds in small quantities. In hindsight, however, without the slag carbonation technology, the Company could not have proposed the joint development on the marine use of slag to the Ministry and the CaO-improved Soil would not have been developed. Therefore, the present development paved the way for the marine application of steelmaking slag in large quantities.

Acknowledgements

The authors would like to express their profound gratitude to the people of Nagoya Plant of Yabashi Industries Co., Ltd. and Tokai Plant Engineering Co., Ltd., as well as to Mr. Akio Uehara of Nagoya Plant of Kyouzai-saiseki Co., Ltd., Mr. Takashi Inoue formerly of the Sangyo Shinko Co., Ltd., and Mr. Yasushi Nishimura of Tokai Kogyo Co., Ltd. for their cooperation in the design and operation of the pilot plant of the rapid slag carbonation process.

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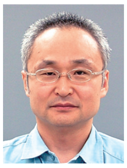

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