UPDATE OF IRON AND STEEL SLAG IN JAPAN AND CURRENT DEVELOPMENT FOR VALORISATION

Tomo ISAWA, Nippon Slag Association

鐵鋼スラグ協会
Nippon Slag Association

一般社団法人 日本鉄鋼連盟
The Japan Iron and Steel Federation

THIRD INTERNATIONAL
SLAG VALORISATION SYMPOSIUM
THE TRANSITION TO SUSTAINABLE MATERIALS MANAGEMENT
19-20 March 2013
Leuven, Belgium

Contents

- Activity of Nippon Slag Association
- Statistics: production and sales of iron and steel slag
- Laws, environmental criteria, sales management

- Development of BOF slag for marine use

Nippon Slag Association

Established in 1978

FOCUS: Iron and steel slag

TARGET: to create Recycling-oriented Society

The primary objectives are:

to promote a better understanding of iron and steel slag,
to position the slag as a viable commercial product and
to pave the way for its stable supply.

MEMBERS

Iron and Steel manufactures (4), and the Assoc./Group of manufactures (2)
Cement and BF cement companies (5)
Slag processing companies (15)

Annual production of 'slag' in Japan (2011)

from **metal manufacture**

million tonnes

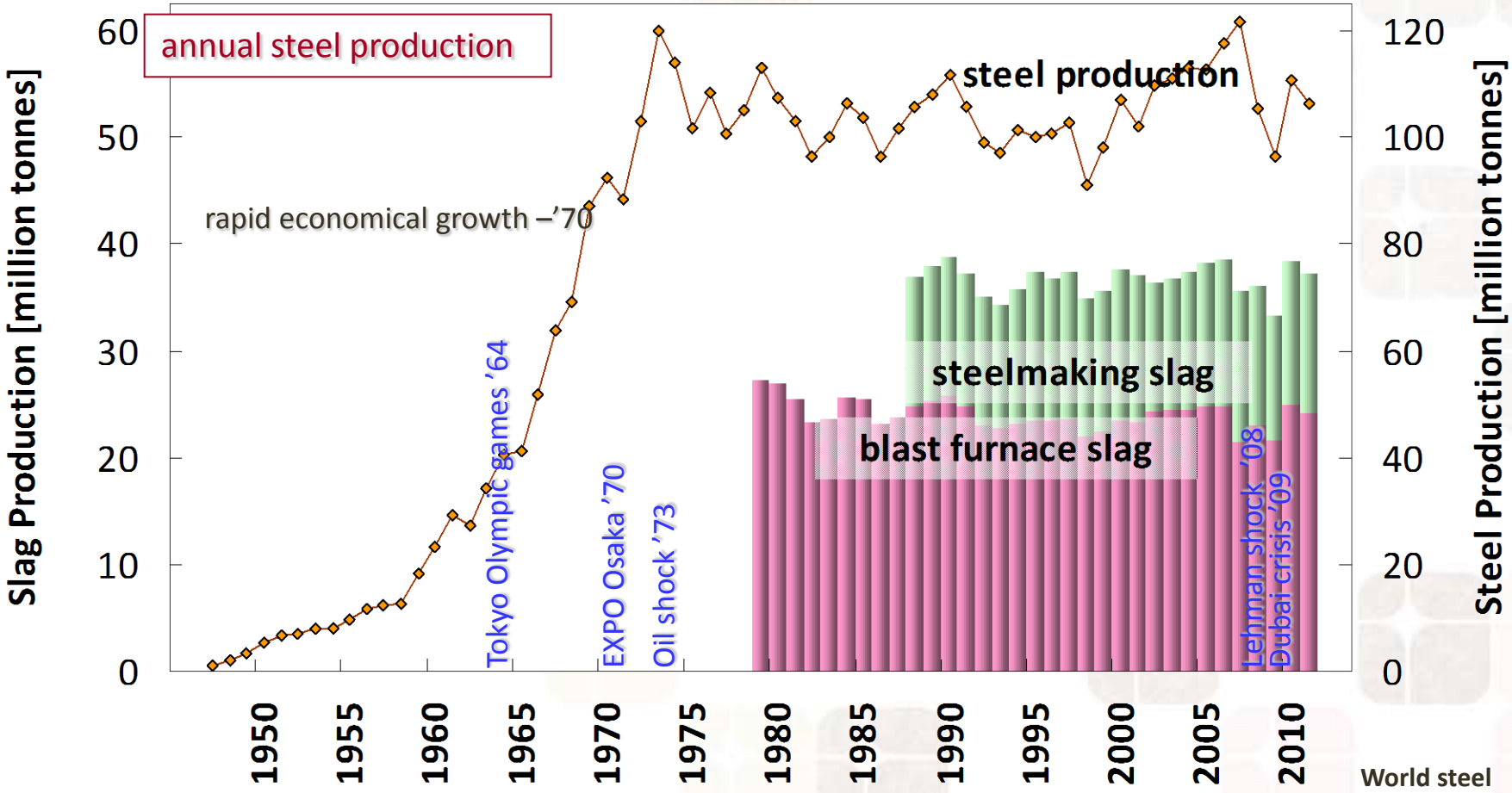
Ferrous	Blast furnace slag	Granulated BF slag	19.5
		Air-cooled BF slag	4.7
	Steelmaking slag	BOF slag	11.3
		EAF slag	2.9
Non-Ferrous	Copper-, Ferronickel-slag etc		5.3

BOF: Basic Oxygen Furnace
EAF: Electric Arc Furnace

from waste treatment

heat-treated, melted/fused waste, sewage sludge	0.8

Slag and steel production in Japan

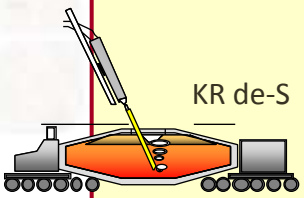


Blast furnace slag	24 million tonnes/yr (～300kg-slag/t-HM)
Steelmaking slag	13 million tonnes/yr (～120kg-slag/t-steel)

Iron and Steel slag in steel manufacture

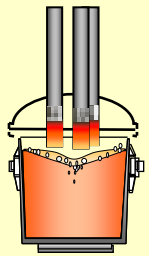
Integrated mill
eg. **BF-BOF-RH/LF**-CC/IC

EAF steelmaking
eg. **EAF-LF/RH**-CC/IC

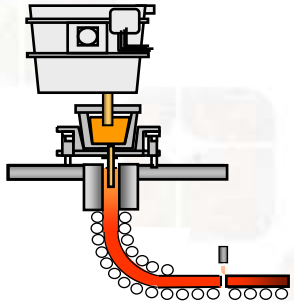


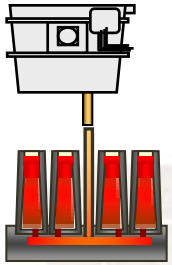
Hot metal pre-treatment

scrap
pig iron
DRI



Secondary Refining
post refining
comp. fine control
temp. adjustment





BF slag

ash from coke
gangue of ore
limestone

Steelmaking slag (BOF, EAF slag)

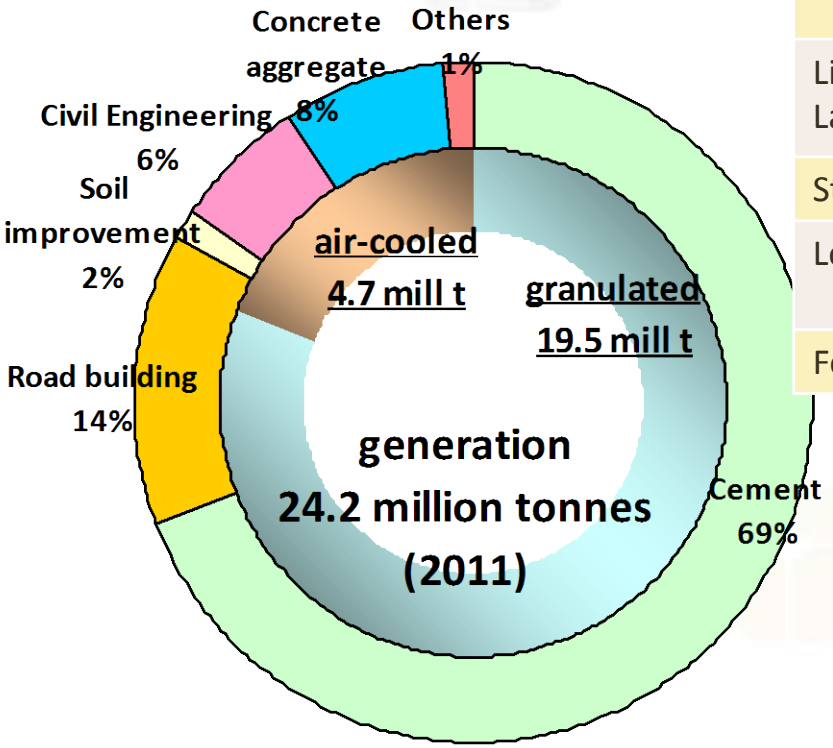
carried-over BF slag (SiO_2, CaO, Al_2O_3, MgO)
oxides of hot metal ingredient (Si, Mn and P)
burnt lime as a flux and iron oxide for refining

Chemical compositions of ferrous slag

Typical chemical compositions of various ferrous slag (%)

		CaO	SiO_2	Al_2O_3	MgO	FeO	S	P_2O_5	remarks
Blast furnace	**Granulated / air-cooled**	**42**	**34**	**13**	**7.4**	**<0.5**	**0.8**	**<0.1**	**%CaO/%SiO_2 =1.2**
BOF SMS		**46**	**11**	**2**	**6.5**	**17.4**	**0.1**	**1.7**	
	Pre de-S	*50*	*10*	*2-10*	*2*	*7*	*1.5*	*<0.5*	reference /JFE steel
	Pre de-P	*35*	*25*	*5*	*5*	*15-25*	*<0.2*	*2.5-5.0*	
	BOF	*45*	*15*	*3*	*5*	*15-20*	*<0.1*	*2.0*	
	LF, etc	*30-40*	*10-15*	*15-35*	*5-10*	*10-25*	*<0.1*	*<0.5*	
EAF	**Oxydising**	**23**	**12**	**7**	**6.8**	**29.5**	**0.2**	**0.3**	
	Reducing	**55**	**19**	**17**	**7.3**	**0.3**	**0.4**	**0.1**	
Rock: Andesite		**6**	**60**	**17**	**2.8**	**3.1**	**-**	**-**	reference
Portland Cement		**64**	**22**	**6**	**1.5**	**3.0**	**2.0**	**-**	reference

Breakdown of BF slag usage



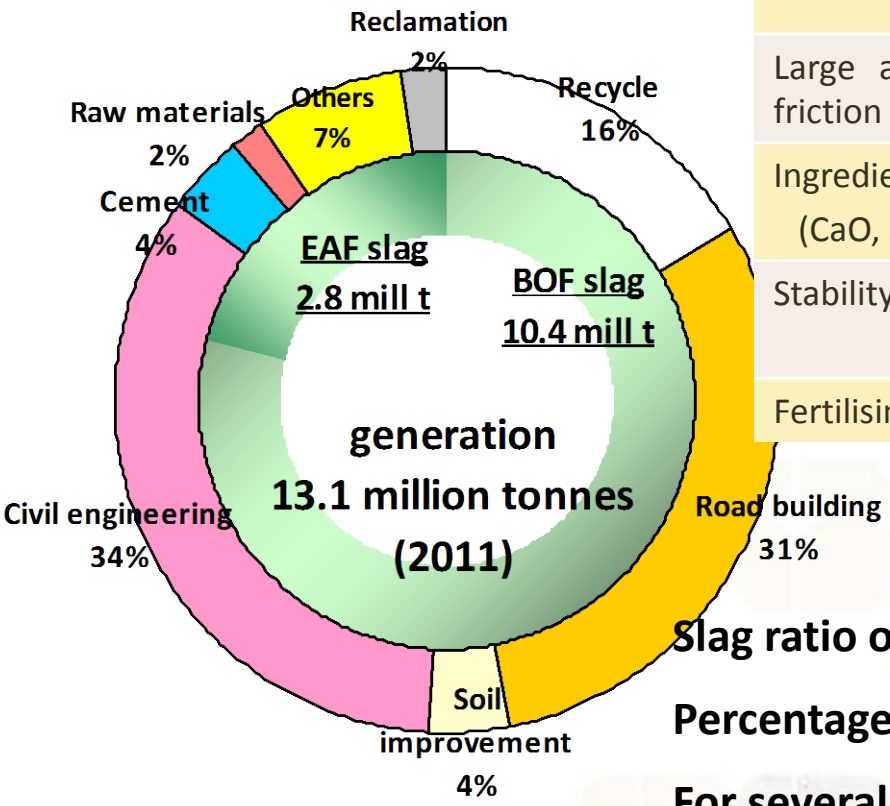
Characteristics	Main Uses (JIS Nos.)
Hydraulicity	Road building (A 5015) Cement (R 5211, R 5210, A 6206)
Lightweight, Permeability, Latent hydraulicity	Soil improvement Backfills in civil engineering
Stability, anti-alkalinity	Aggregates for concrete (A 5011-1)
Low content of Na_2O, K_2O	Clay as a raw material of cement clinkers
Fertilising ingredient	CaO and SiO_2 source for fertilizer

Merit of BFS cement use in CO_2 emission (kg-CO_2/t)

Items	Portland Cement	PBFC	Reduction	
Electricity	77	55	22	29%
de-CO_2 (limestone)	510	294	216	42%
Combustion	271	159	112	41%
Delivery, etc	38	18	20	
Total CO_2 emission	896	526	370	41%

Nat. Inst. for Land and Infrastructure Management, Project Research Report of NILIM 36, Feb.2012.

Breakdown of steelmaking slag usage



Characteristics	Main Uses (JIS Nos.)
Hardness, anti-wearing + Hydraulicity	Aggregate for asphalt concrete (A 5011-1) Road building (A 5015)
Large angle of internal friction	Civil engineering, soil improvement (SCP)
Ingredient (CaO, SiO_2, Al_2O_3)	Raw material for cement clinker
Stability (EAF slag)	Aggregates (anti alkali-silica reaction) (A 5011-4)
Fertilising ingredient	CaO and SiO_2 MgO, FeO, (P_2O_5) source

SCP: sand compaction pile

Slag ratio of BOF and EAF is about 120kg/t-steel

Percentage of reclamation is 2% (40% in 1980)

For several cases, a risk of the expansion and the alkali risk should be considered depending on a use.

Management of slag expansion

Expansion of BOF slag in service causes trouble on road surface

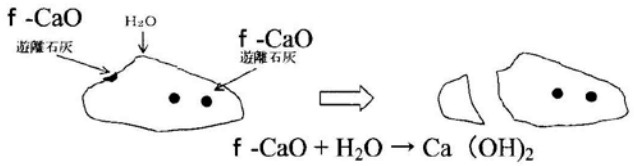
Measurement of expansion

Evaluation of expansion and standardisation as an engineering material

road building material

Management and suppression of the expansion

steam ageing for accelerated treatment



JIS A 5015 (revised March 2013)

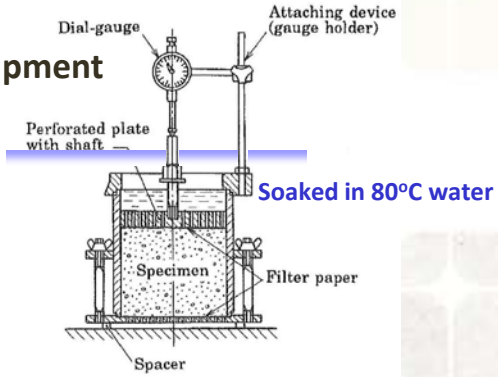
1) Accelerated test

2) Criteria for expansion stability

for road base: less than 1.5%

for asphalt aggregate: less than 2.0%

Expansion measuring equipment



Legal Position of Iron and Steel Slag

Basic Environment Law
the Basic Law for Establishing the Recycling-based Society

Waste Management and Public Cleaning Law (1970),

definition: 'Waste is a filthy or discarded object in a solid or liquid form …'
category: general waste and 19 industrial wastes, including **"slag"**
Whether "**waste or not**" is to be evaluated by comprehensive consideration of 5 factors:
1) **properties** of the object, 2) **states and conditions** when discharged,
3) procedure of **handling**, 4) **economical value**, and 5) **intention of possessor**.

(Notifications for the application of law, by Ministry of the Environment, '71, '05, '05)

Law of Promotion of Effective Utilisation of Resources (2000):

Promotion of **3Rs**: reduce, reuse and recycle
Steel industry is one of "5 designated resources-saving Industries", and is required to promote **the reduction of, and the effective use of ferrous slag as by-products**.

Nippon Slag Association takes the situation that
Iron and Steel slag is not a waste as far as it is used commonly, effectively and environmentally correctly.

Quality Standards for Environment

Standard for primary heavy metals:

substance	CaO for soil pollution		harbour use only Elution	for seabed [mg/litre]
	Content [mg/kg]	Elution [mg/litre]		
Cadmium (Cd)	150	0.01	0.03	0.1
Total cyanide (t-CN)	50	ND	-	1
Lead (Pb)	150	0.01	0.03	0.1
Chromium hexavalence (Cr^{6+})	250	0.05	0.15	0.5
Arsenic (As)	150	0.01	0.03	0.1
Total Mercury (t-Hg)	15	0.0005	0.0015	0.005
Alkylmercury (R-Hg)	-	ND	-	ND
Selenium (Se)	150	0.01	0.03	0.1
Fluorine (F)	4,000	0.8	15	15
Boron (B)	4,000	1	20	

Interim criteria is applied to harbour use

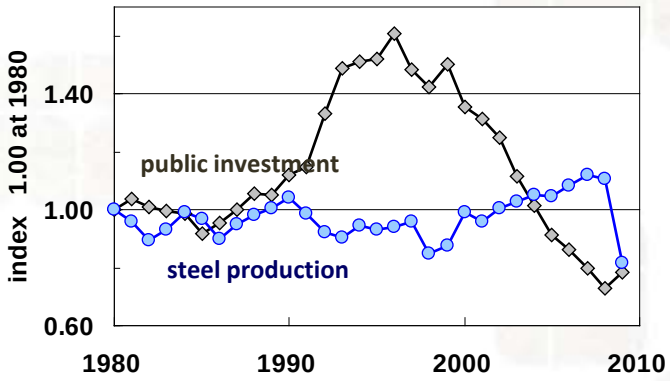
Sales management

Social requirement to slag products is not optimistic.

Disagreement of supply/demand balance
- decrease of public construction investment
- competition with other recycle materials

Actualisation of environmental risks
- lack of understanding of the slag and its quality control

Unfavourable feeling to recycle material
- environmentally consciousness of public
- need for communication of slag information



Not only R&D for new applications and technology of quality assurance, but also sales management are necessary; ensuring the appropriate utilisation of ferrous slag product, and preventing problems arising from it.

The Guide Line includes:

- Quality Control and Assurance Methods for Slag Products
- Compliance for Order Acceptance & Delivery of the products
  - Evaluation of environmental influence around the site before sales
  - Judgment as to the adequacy of Utilisation
  - Customer follow-up during construction and after use
- Countermeasures in case of problems
- Internal and external audit for confirmation of compliance

New application of steelmaking slag

The situation of slag sales in Japan

Blast furnace slag has established a stable position for cement industry.
Its availability is well known, though the public education is still necessary.

Steelmaking slag need further development of new applications to compete with other recycle materials.
These are the tasks that we should intensively settle while confirming the environmental impacts:

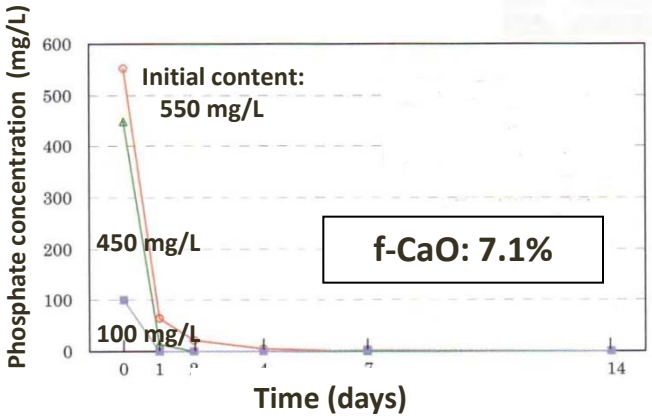
- to utilise the characteristics of slag to the maximum
- to overcome the disadvantageous points of slag, and
- to educate the advantage of slag to the public with practical examples.

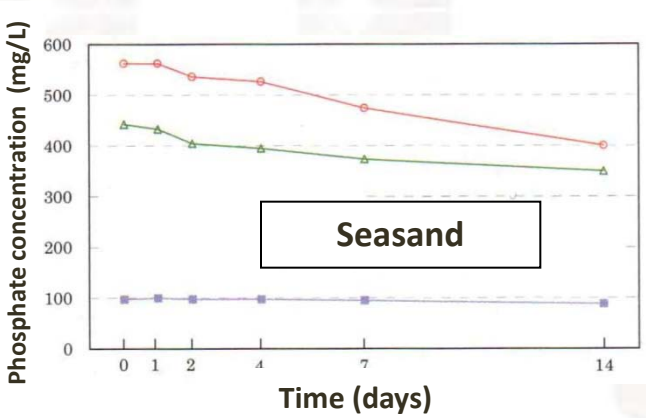
Characteristics for steelmaking slag

characteristic	explanation	
Specific gravity	2.2 – 3.7 g/cm^3	Higher than natural aggregate
Chemical composition	CaO, SiO_2, FeO, Al_2O_3	Similar to natural aggregate Possible expansion and pH increase due to free lime (CaO)
Hydraulicity	Weak cement property when contacting with water	
Environmental aspects	Fulfill the environmental requirement (heavy metals)	
Expansion	Consideration may be necessary depending on application	
Clarification effect	Strong affinities with Phosphate and sulphide	
Improvement of dredged soil strength	BOF slag containing high concentration of free lime improves mechanical strength of dredged soil	
Influence of alkali	Untreated BOF slag may cause rapid increase of pH, though alkali is mitigated by magnesium ions in seawater in long-term.	

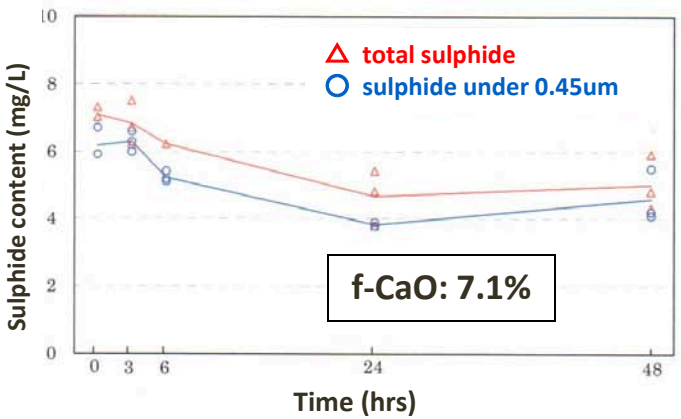
Clarification effect: P and S absorption

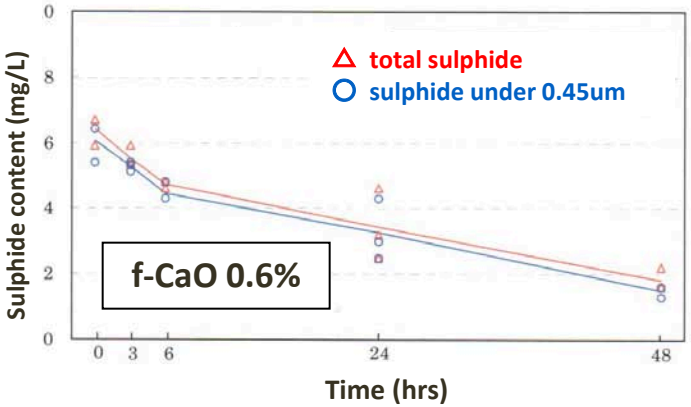
Phosphate:
positive relation between absorption and f-CaO content



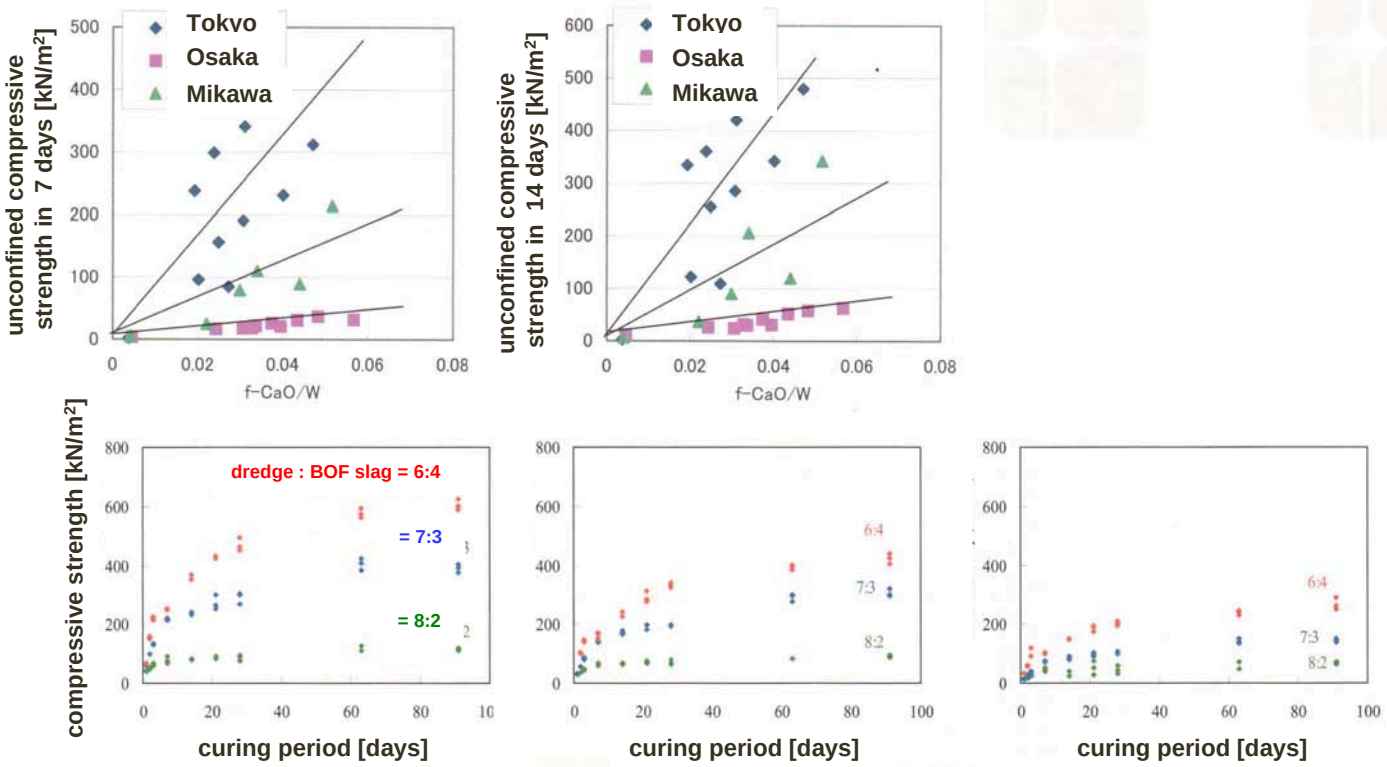


Sulphide:
negative effect of f-CaO on the suppression of H_2S





Improvement in mechanical properties of dredged soil



Initial fluidity: 10cm(left), 15cm(mid), 20cm(right)

Physical effect:
decrease in moisture content of the mixture
improvement in particle distribution
Chemical reaction: in short period hydro reaction

Influence on pH and white turbidness

Possible influence of BOF slag for the marine application

High pH near the slag

$$CaO + H_2O \rightarrow Ca(OH)_2 \rightarrow Ca^{2+} + 2\,OH^-$$

White turbidness during construction

$$Mg^{2+}(\text{in seawater}) + 2\,OH^- \rightarrow Mg(OH)_2$$

In order to reduce environmental impact of alkali

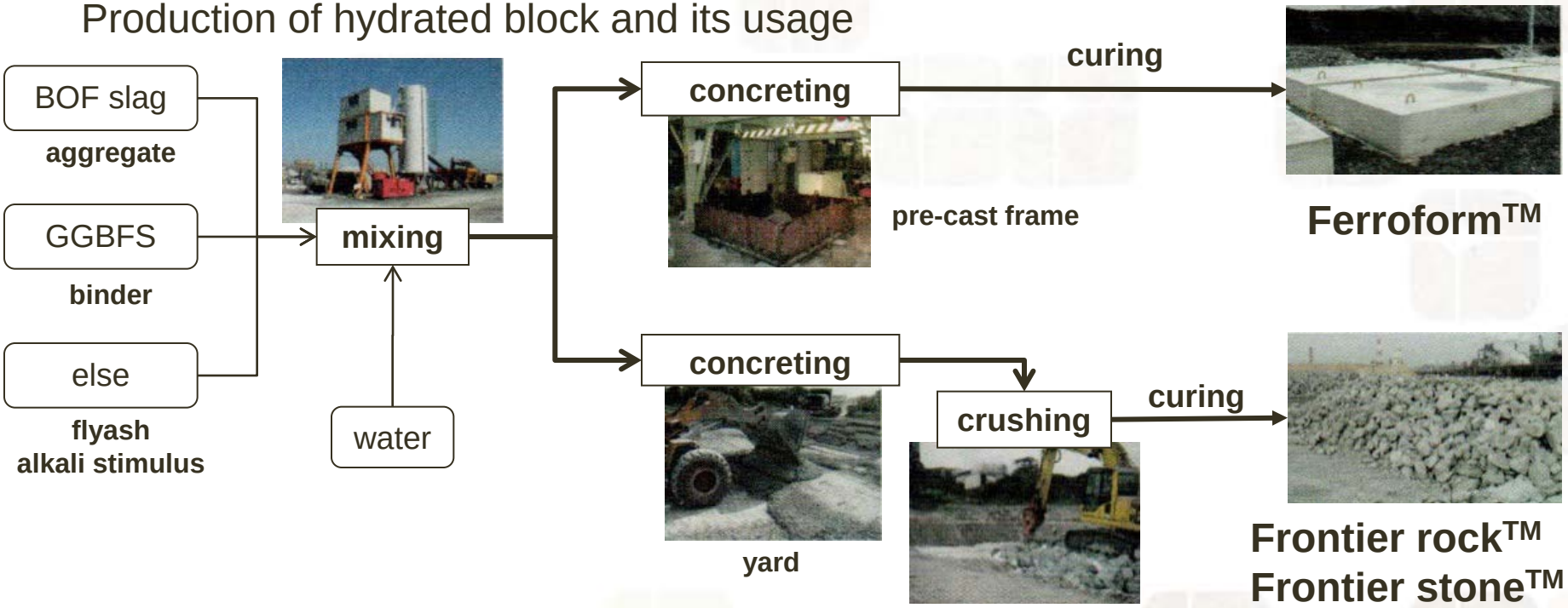
decrease the area contacting with water

lower the activity of free CaO

		Size *coarse* ⟵ ⟶ *fine*	
Size control		Particle distribution Elimination of powder	
		Steel Slag hydrated block	
Chemical reaction	carbonation	Marine block	Rapid Carbonation
	reaction with soil		Mixture with dredged soil (C-S-H, C-A-H reaction)

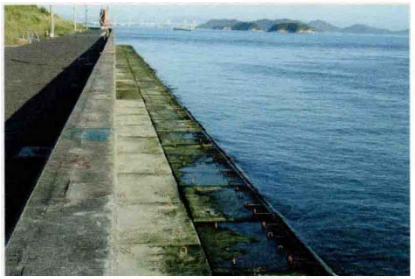
Steel Slag Hydrated Block / Stone

Production of hydrated block and its usage



Wave breaker

Ferroform

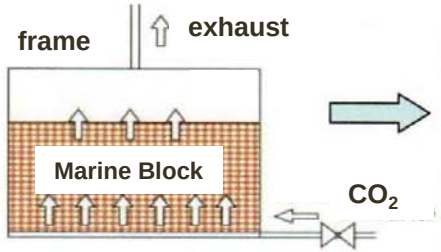


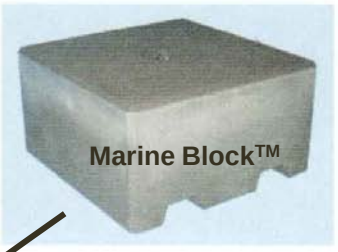
Artificial stone/rock

Algae construction

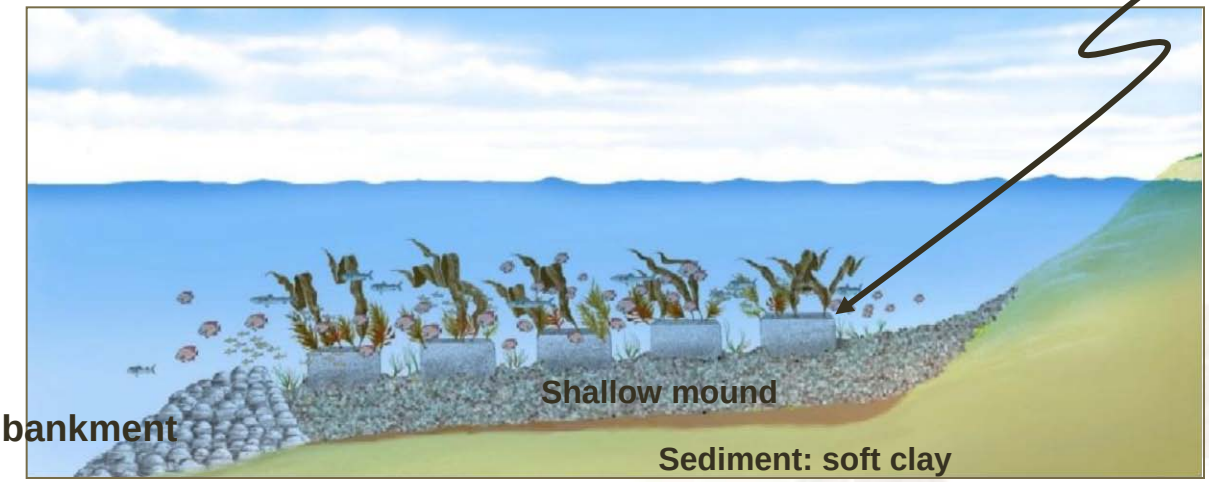
Algae block of carbonated slag matrix

Restoration of the marine environment





Production of marine block™



Micropore $CaCO_3$

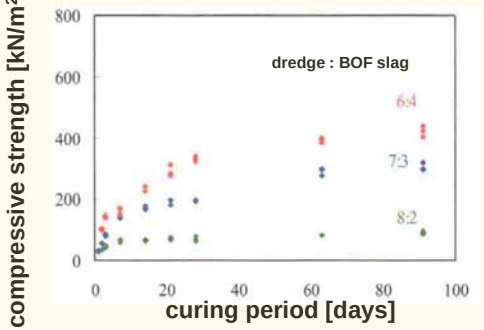
Microstructure of MB

Properties control of dredged clay

Dredged clay
q_u = 0 kN/m²

BOF slag
high f-CaO

Improvement in strength



Dehydration by free lime
Decrease in fluidity by C-S-H formation

Mitigation of pH impact

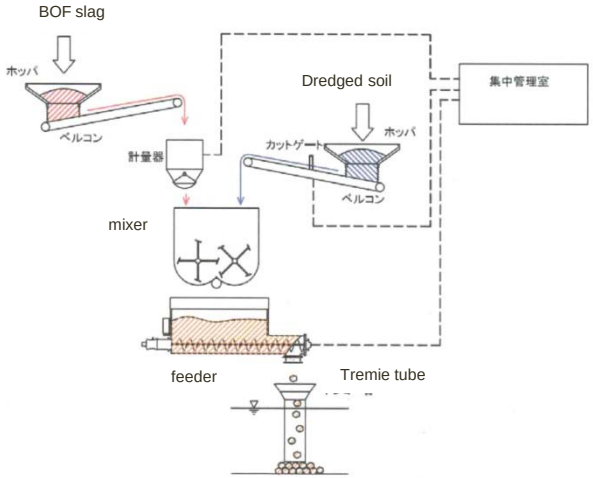
pH = 9.8 in seawater

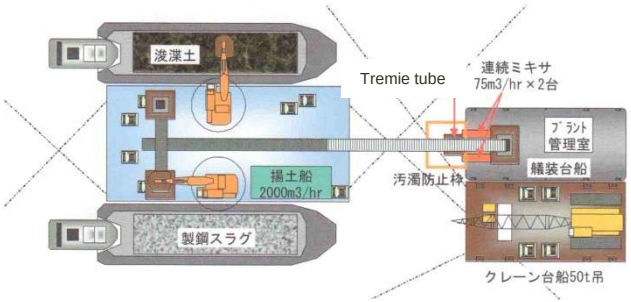
pH = 8.2

C-S-H reaction consumes f-CaO

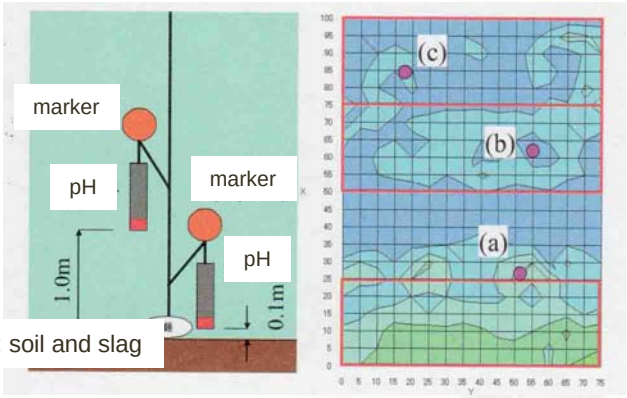
Clarification effect (experimentally confirmed);
absorption of excess nutrition (phosphate)
suppression of harmful gas (H_2S)

Influence on pH of the construction

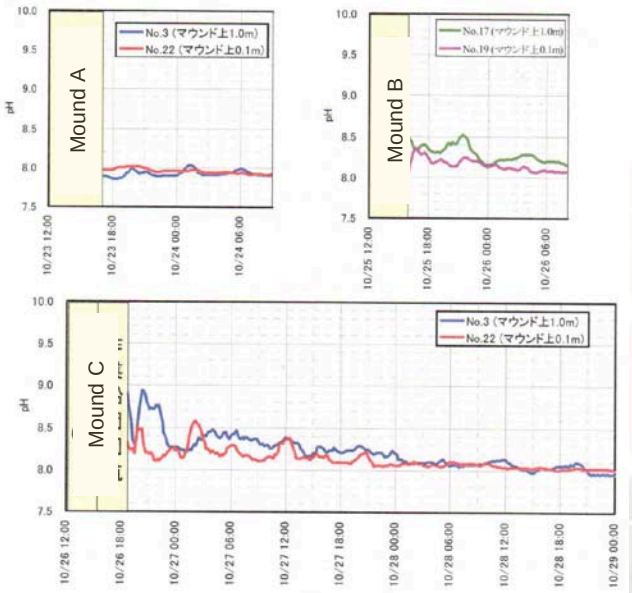




Shallows construction with continuous mixing with dredged soil and dumping to the site



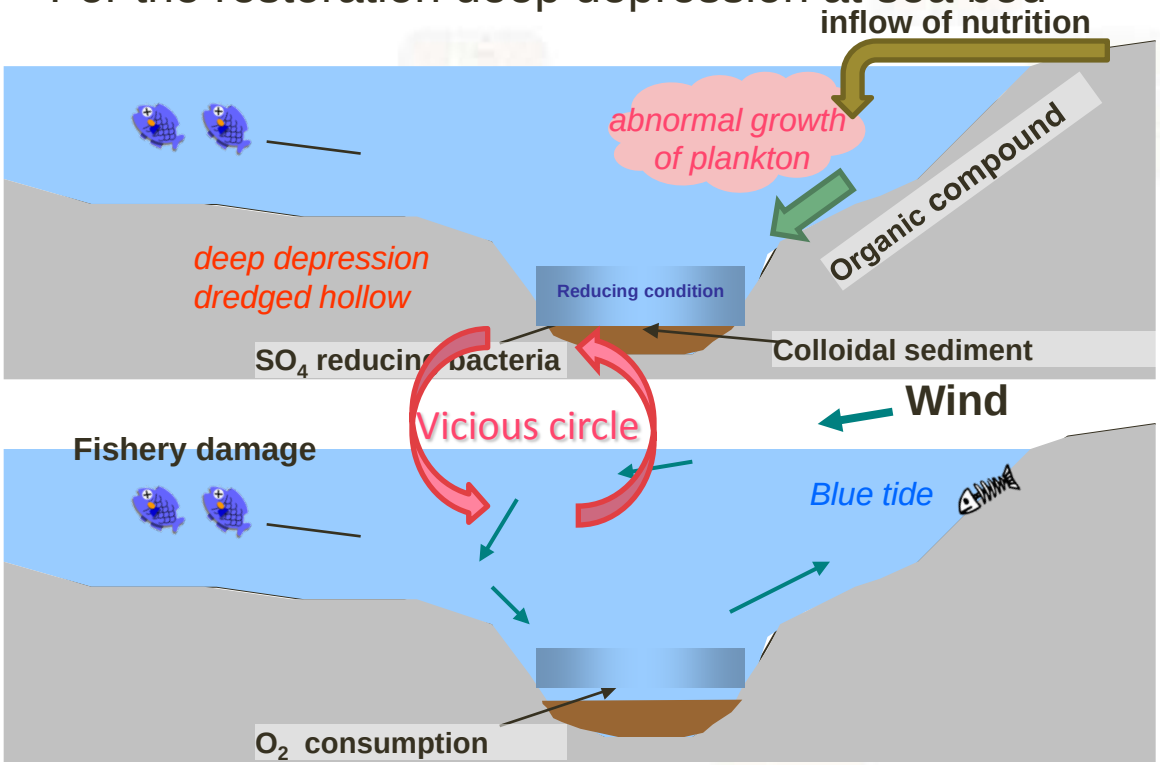
Mixture: soil and slag



pH increase last several hours and recovered soon

Backfill of the depression at seabed

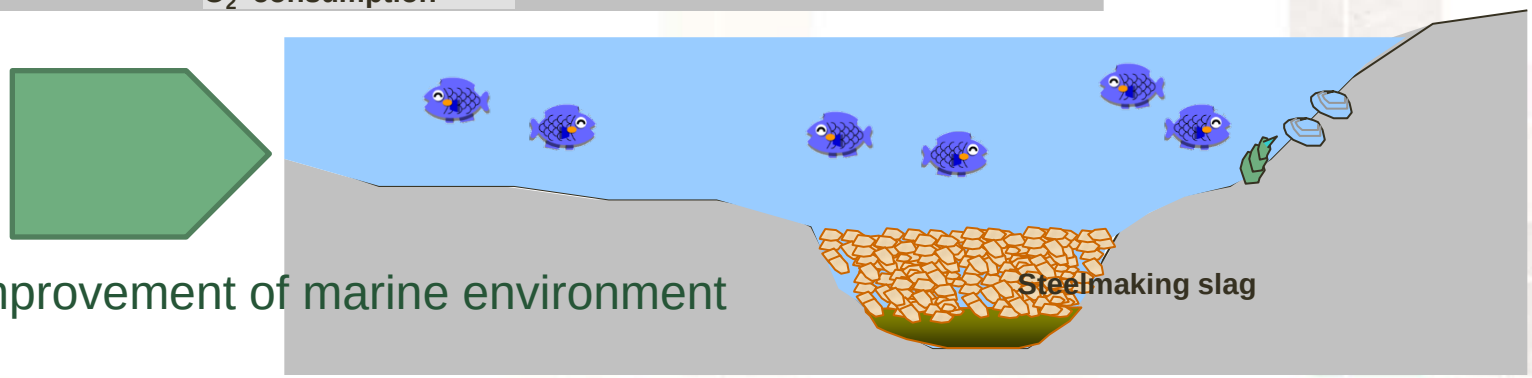
For the restoration deep depression at sea bed



Loss of *Philippinarum*

September 1985	30,000 t
September 1986	1,400 t
August 1988	4,200 t
September 1994	2,700 t

by Chiba Pref. Fisheries Exper.Sta.



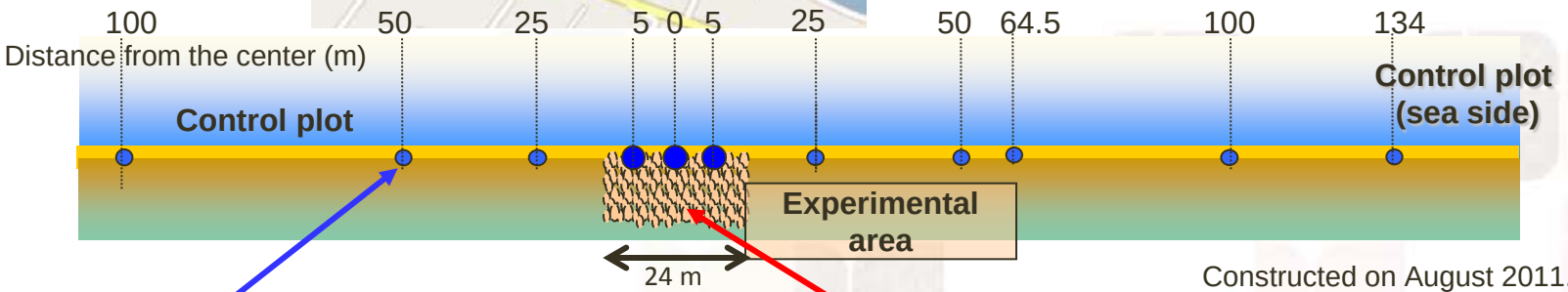
Improvement of marine environment

Suppression of H_2S odour in harbour

Construction area : Fukuyama inner harbour (100 m width x 2.2 km length x 2-4 m depth)
Experimental site 24 m×18 m

Steelmaking slag : a particle size adjusted to 5-25 mm
JFE Steel West Japan Works (Fukuyama)

T.Fe	SiO_2	CaO	Al_2O_3	MnO
17.5	29.3	33.0	6.0	8.7
MgO	**P_2O_5**	**TiO_2**	**S**	
4.9	3.8	1.2	0.13	



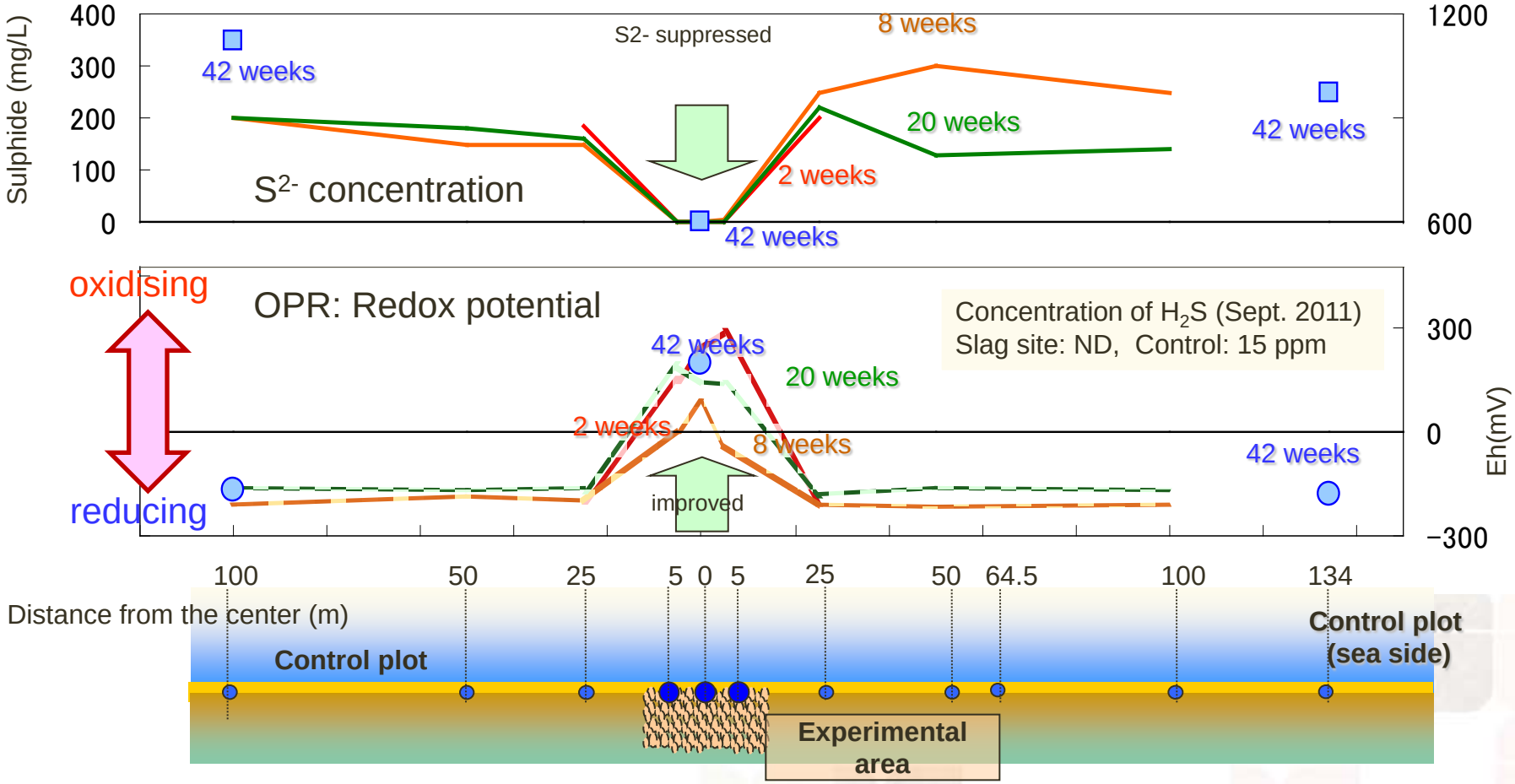
Constructed on August 2011.

Schematic view of measuring positions

interstitial of sediment

interstitial of slag

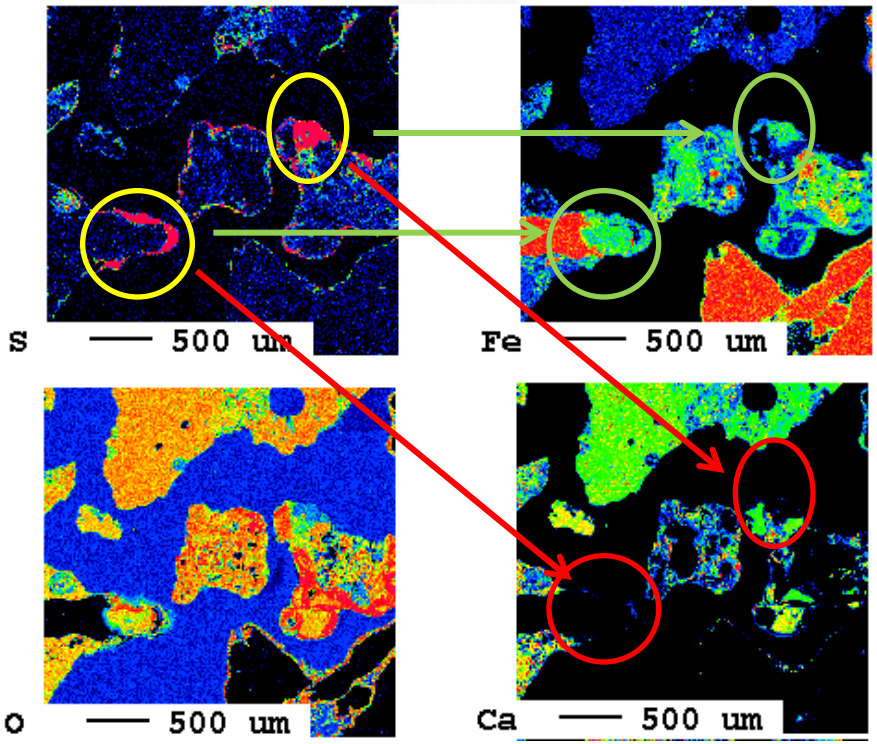
Water quality in the interstitials



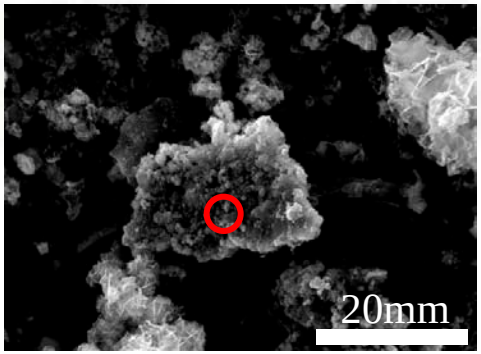
Water qualities (sulphide concentration and ORP of the water) are remarkably improved and the effects last for 10 months.
The pH above the seabed are constant (ca. pH=7.3) through the experiment.

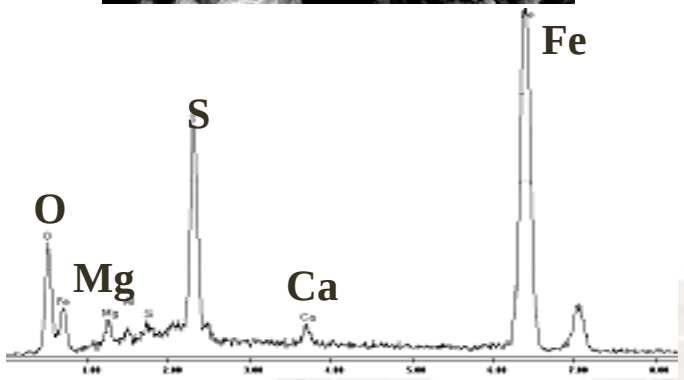
Mechanism of sulphide capture

Cross section of suspended solid



SEM image of suspended particles

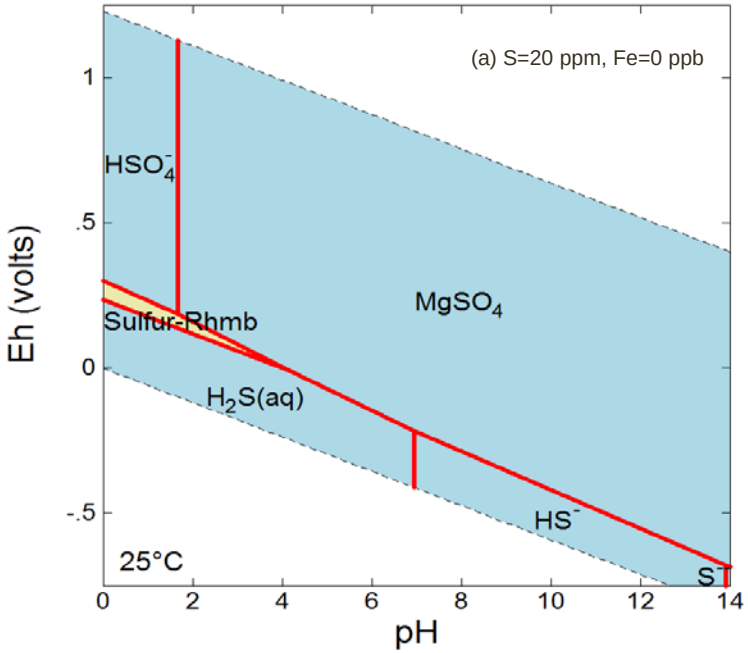


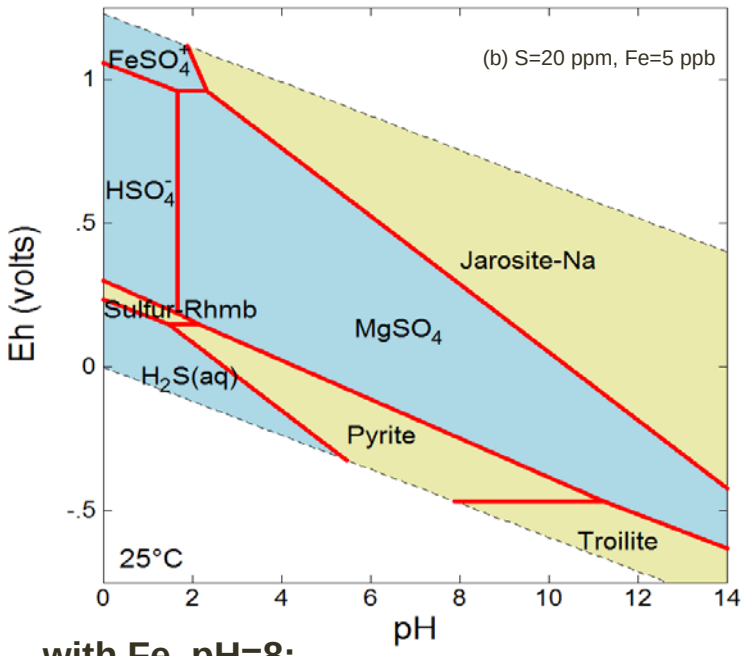


The area sulphur concentrate corresponds to the area iron exists, though Ca has weak correspondent to sulphur.
Particles of iron sulphide were detected from solid suspension in seawater.

EPMA : Eectoron Probe MicroAnalyzer

Sulphide capture by BOF slag

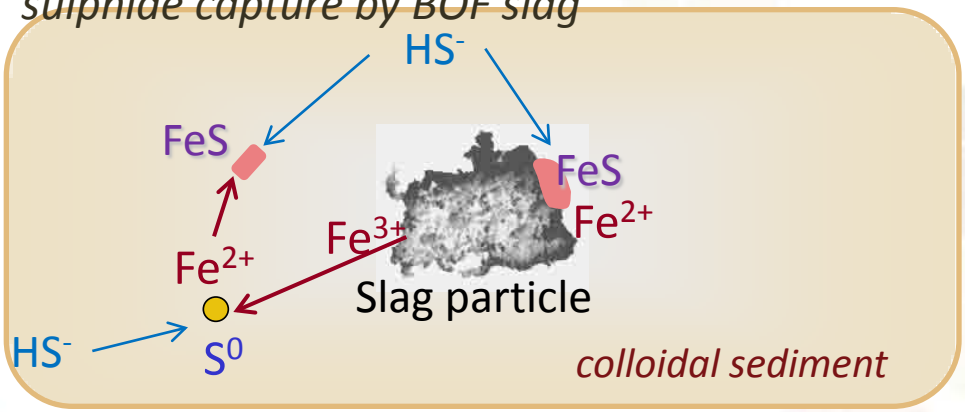




with Fe, pH=8:

FeS / FeS_2 in low ORP, and S/SO_4^{2-} in high ORP.

sulphide capture by BOF slag



$HS^- + Fe^{2+} \rightarrow FeS + H^+$

$HS^- + 2Fe^{3+} \rightarrow S^0 + 2Fe^{2+} + H^+$

Restoration of the marine environment

Artificial seaweed bed, shallow bottoms, tidal flats

Formation of seaweed beds, shallow bottoms & tidal flats makes cradle of fish and shellfish

Concluding remarks

In order to contribute the realisation of recycling-oriented society, our activity is focusing on:

to promote a better understanding of iron and steel slag,
to position the slag as a viable commercial product and
to pave the way for its stable supply.

The restoration of the marine environment with BOF slag is a big approach that substantiate the maximum utilization of slag's characteristics. Development of seashore and prevention of disasters were the principal objectives, but the restoration of lost sea area environment will be recognised as an important theme in future as well. These developments and proposals meet social needs, and they promote public confidence for the slag.

Nippon Slag Association contributes to sustainable growth of steelmaking industry through these activities.

Thank you for your attention.

Acknowledgement: Figures of the marine use were used thanks to the permission of JISF.