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Assessment of ecological impact of basic oxygen furnace slag used as a fill material on the surrounding environments

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Research scope and objective

- Basic oxygen furnace slag (BOF slag, converter slag) from steel-making industry is physically a good material as construction aggregate, but it contains some heavy metals originating from ores and fluoride from a process additive (CaF_2).
- Especially when BOF slag is used as a fill material in soil, such compounds may release into the soil and may increase soil pollution levels of the compounds.
- In addition, potential risk to the receptors (human and ecosystem) nearby resulting from the released compounds needs to be identified for safe and stable re-use of BOF slag.

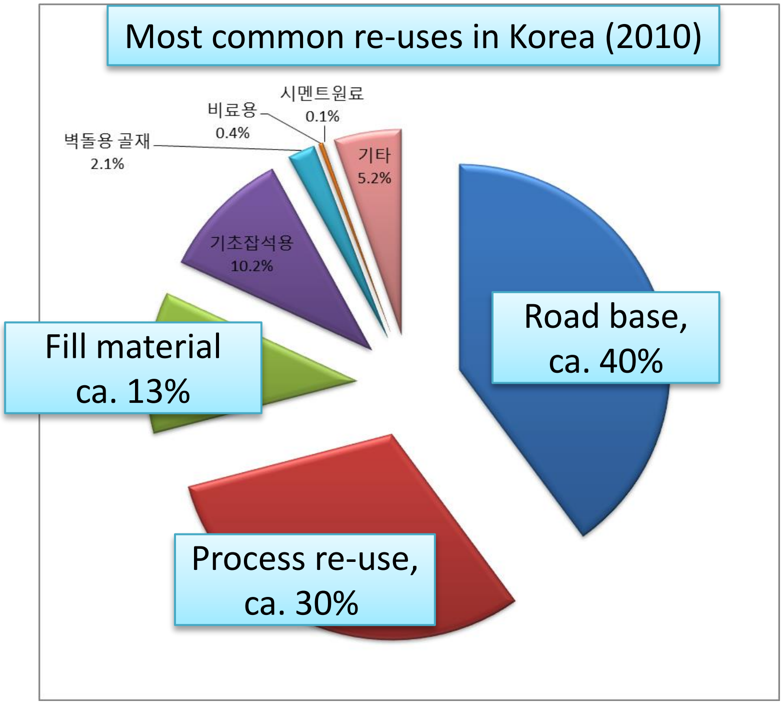
➢ This study aims to…

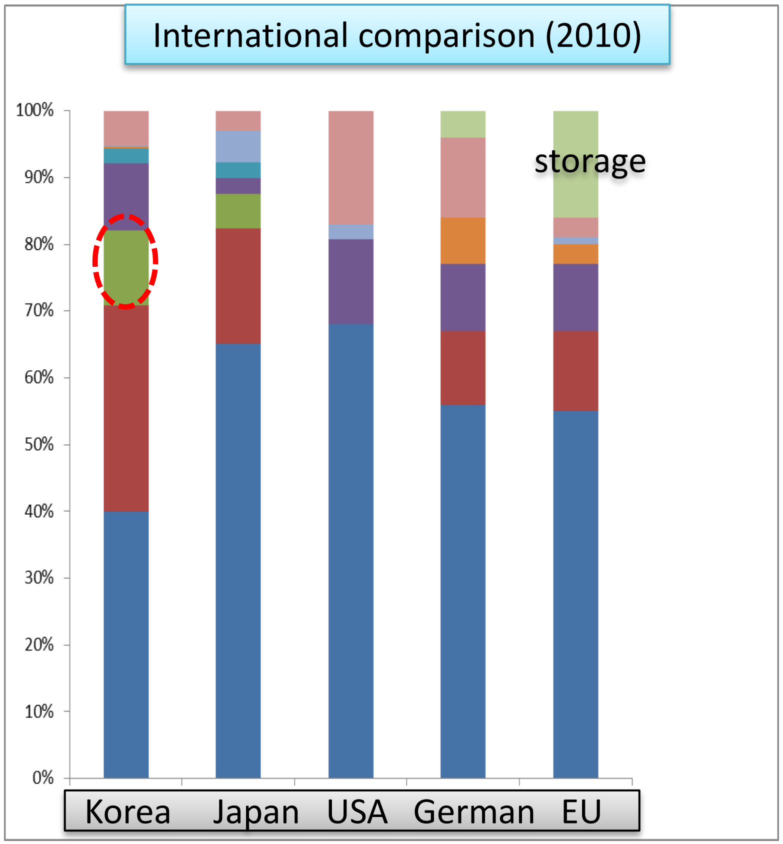
1) determine the extent of release of the potential soil pollutants from BOF slag

2) estimate the long-term leaching behaviors of the pollutants in soil

3) characterize potential risk posed by BOF slag and its leachate

Re-use statistics of basic oxygen furnace slag





- Globally, re-use as a road base material is the most popular.
- In Korea, re-use as a fill material (i.e., to make industrial land) occupies more than USA and EU countries.

Composition of steel-making slags

Composition	Blast furnace slag (%)	Steel-making slag		
		Basic oxygen furnace slag (%)	Electric arc furnace slag (%)	
			Oxidizing slag	Reducing slag
CaO	41.6~43.5	36.4~52.2	13.9~38.8	45.0~51.0
SiO_2	33.4~35.5	7.80~13.8	14.1~17.7	23.2~27.0
Al_2O_3	13.6~19.8	1.20~3.00	6.30~12.2	13.0~9.00
T-Fe	0.30~1.22	17.5~38.1	21.2~47.0	1.50~2.15
MgO	3.84~6.70	0.80~9.60	2.90~6.50	7.00~9.90
S	0~1.00	0~0.07	0~0.09	0~0.50
P_2O_5	-	0~3.30	0~1.20	0~0.03
TiO_2	0~1.30	0~1.16	0~0.80	0~0.70
K_2O	0~0.44	-	0~0.22	0~0.06
MnO	0~0.50	0.30~5.30	2.50~7.90	0.50~1.00
SO_3	0~2.85	0~0.30	0~0.06	0~1.10
Na_2O	0~0.20	-	0~0.52	0~0.35
Major elements	$CaO-SiO_2-Al_2O_3$	$CaO-SiO_2-FeO$	$CaO-SiO_2-FeO-Al_2O_3$	$CaO-SiO_2-Al_2O_3$

Comparison with leaching test methods

● Various leaching test methods

Method	L/S ratio	Leaching solution	Agitation
Korea	1:10	distilled water (pH 5.8~6.3)	6 hr / RT / 200 rpm
TCLP (US EPA)	1:20	acetic acid solution (pH 2.88)	18 hr / 23±2℃ / 30 rpm
D 3987 (ASTM)	1:20	distilled water	18 hr / 18~27℃ / 30 rpm
EN 12457 (EU)	1:2	deionized water	24 hr / 20±5℃ / 10 rpm

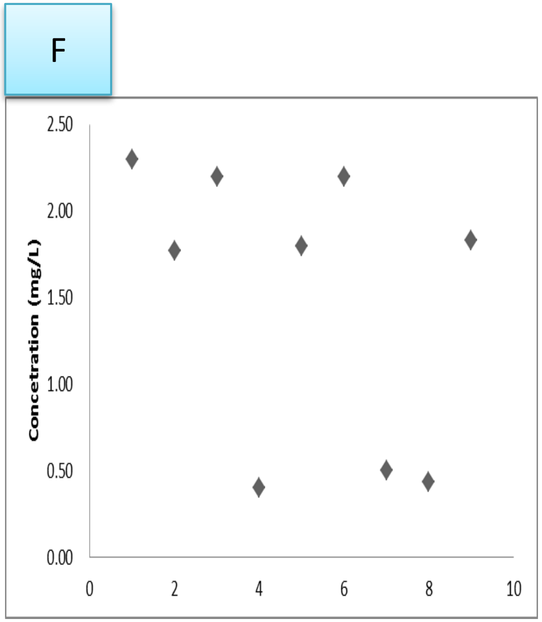
● Leaching test results

(unit: mg/L)

Method	Final pH	F	Ni	Zn	As	Cd	Cu	Cr^{6+}	Hg	Pb
Korea	12.9	2.233	ND[1)]	0.002	ND	ND	ND	ND	ND	ND
TCLP (US EPA)	12.7	3.667	ND	ND	ND	ND	ND	ND	ND	ND
D 3987 (ASTM)	13.0	3.528	ND	0.004	ND	ND	ND	ND	ND	ND
EN 12457 (EU)	12.9	2.423	ND	0.042	ND	ND	0.011	ND	ND	ND

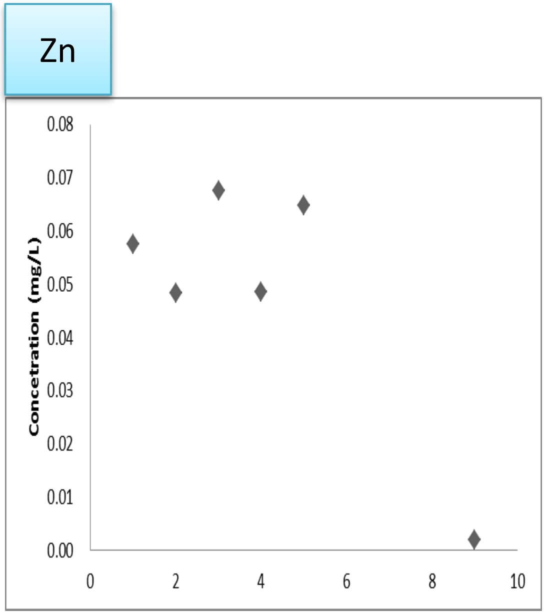
[1)] Ni: 0.002 mg/L, Zn: 0.002mg/L, As: 0.004 mg/L, Cd: 0.002 mg/L, Cu: 0.008 mg/L, Cr^{6+}: 0.01 mg/L, Hg: 0.0005 mg/L, Pb: 0.04 mg/L

- **Detection frequency**



detected 9 out of 9 samples

- Avg. 1.493 mg/L
- Max. 2.30 mg/L
- Min. 0.40 mg/L



detected 6 out of 9 samples

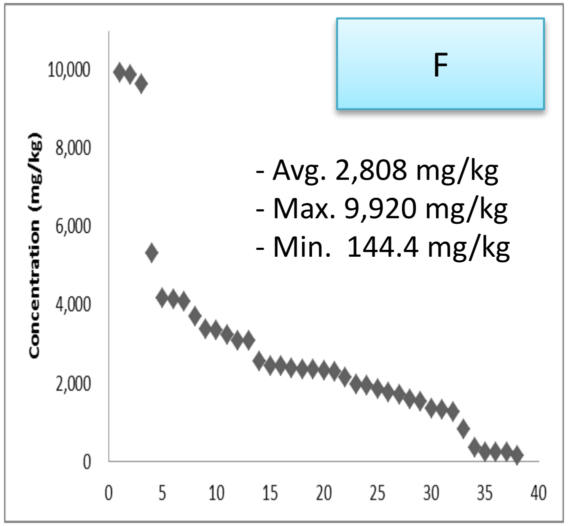
- Avg. 0.032 mg/L
- Max. 0.067 mg/L
- Min. 0.02 mg/L

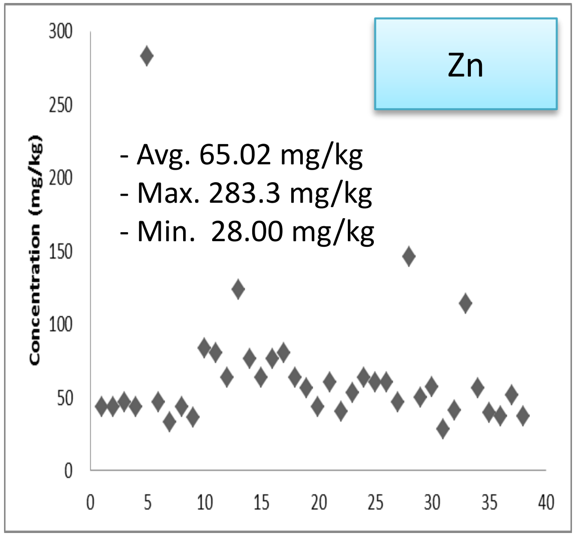
Total concentrations

- When used as a fill material, BOF slag is considered as soil and thus needs to comply Korean soil standards.
- Legally in Korea, concentrations of inorganics in soil is determined by *aqua regia* digestion method (i.e., HNO_3:HCl, 1:3 (v/v)).

(unit: mg/kg)

	F	Ni	Zn	As	Cd	Cu	Cr^{6+}	Hg	Pb
Maximum conc. (n=38)	9,920	23.10	283.3	2.380	1.110	15.15	7.600	ND[1)]	24.95
Korean soil standards									
Region 1	400	100	300	25	4	150	5	4	200
Region 2	400	200	600	50	10	200	15	10	400
Region 3	800	500	2,000	200	60	2,000	40	20	700



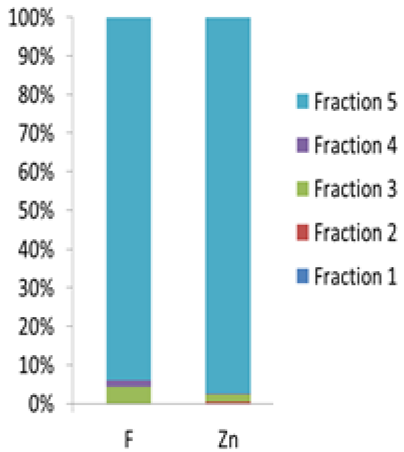


- *Detection frequency: Both compounds were detected in all samples.*

Sequential extraction of BOF slag

Tessier's method(1979) *– usually for cations*

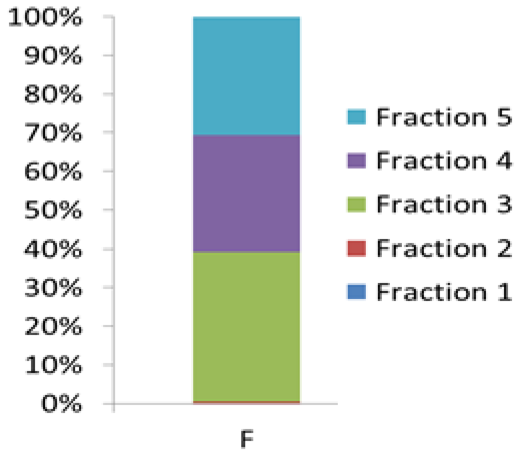
Fraction	Extractant
1) Exchangeable	$MgCl_2$,
2) Bound to carbonates	NaOAc
3) Bound to iron and manganese oxides	NH_2OH-HCl in 25% (v/v) HOAc
4) Bound to organic matter	① HNO_3 and H_2O_2 ② H_2O_2 (pH 2.0 with HNO_3) ③ NH_4OAc in 20% (v/v) HNO_3
5) Residual	HNO_3, HF, H_2O_2



Most seemed to be present as residual forms

Wenzel's method (2001) *– developed for oxyanions*

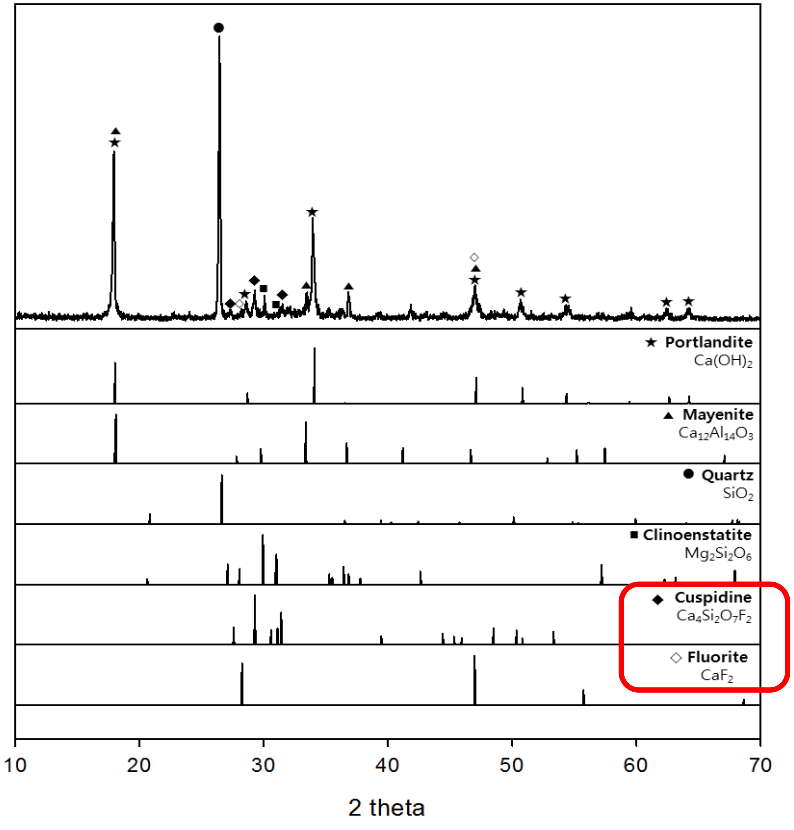
Fraction	Extractant
1) Non-specifically bound	$(NH_4)_2SO_4$
2) Specifically bound	$(NH_4)H_2PO_4$
3) Amorphous hydrous oxide bound	NH_4-oxalate buffer
4) Crystalline hydrous oxide bound	NH_4-oxalate buffer + ascorbic acid
5) Residual	HNO_3, HF, H_2O_2



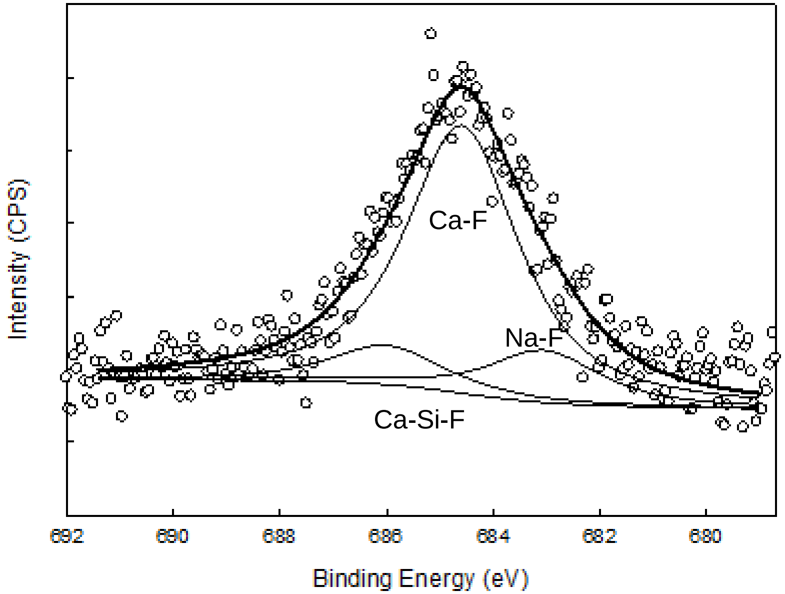
Mixture of oxides-bound and residual forms

Chemical forms analysis

- XRD analysis with Kanvara reactor slag with 9,920 mg/kg of F confirms the presence of minerals containing fluoride such as fluorite (CaF_2, original mineral) and cuspidine (secondary mineral)
  - *Cuspidine is a secondary mineral formed at over 1,000 ℃ in the presence of CaF_2, CaO, SiO_2 with the ratio of 1:3:2 (Watanabe et al., 2000)*
- XPS data confirm their presence and relative contents.



Species	Binding energy (eV)	Relative content (%)
Cuspidine (Ca-Si-F)	686.00	10.95
Fluorite (Ca-F)	684.58	74.48



Prediction of long-term leaching

- Once used as a fill material, the site receives rainfalls continuously, and thus leaching behavior of inorganics from BOF slag may be different from that expected based on batch leaching tests.
- "Percolation-controlled scenario" was employed for long-term leaching prediction.

$$E_{max}(J\,yr) = \frac{E_{max}(L/S=10)\cdot\left(1-e^{-\kappa\cdot\frac{J\cdot N_i}{d\cdot h}}\right)}{\left(1-e^{-\kappa\cdot 10}\right)}$$

E_{max} (J yr): maximum allowable emission per *J* years (mg/kg)

E_{max} (L/S=10): maximum acceptable emission till L/S=10 (mg/kg)

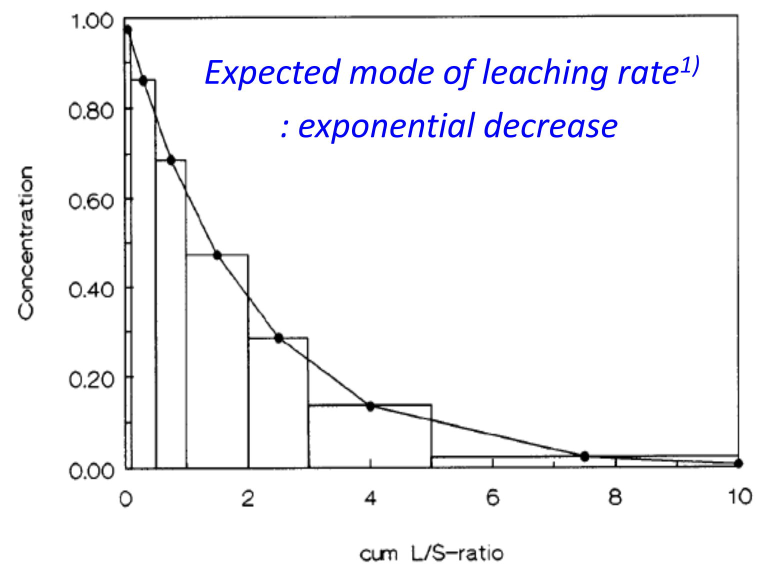
κ : constant (measure of the rate of leaching) (kg/L)

J : period of prediction (year)

N_i: infiltration (m/year)

d: dry density of the construction material (kg/m³)

h: total thickness of the construction layers which consists of roughly the same construction material (m)



[1)] Rate of leaching derived from continuous leaching column test

- Major parameters for percolation-controlled scenario prediction

  ✓ rate of leaching (κ): determined with the slag re-used (i.e., Kanvara reactor slag with 9,920 mg/kg of F)

  ✓ infiltration rate at the site where re-used: 19.49 cm/year (default value in Korea)

  ✓ depth of filling: 4 m

  ✓ prediction period: 100 years

  ✓ dry density of filling material: 1,880 Kg/m^3

➢ κ values derived from column experiment

	F	Ni	Zn	As	Cd	Cu	Cr^{6+}	Hg	Pb
E_{max}(L/S=30), mg/kg	919.9	0.523	2.095	0.376	0.138	0.314	ND	ND	0.258
Leaching rate (κ)[1)]	0.37	0.17	0.29	0.18	0.14	0.27	-	-	0.27

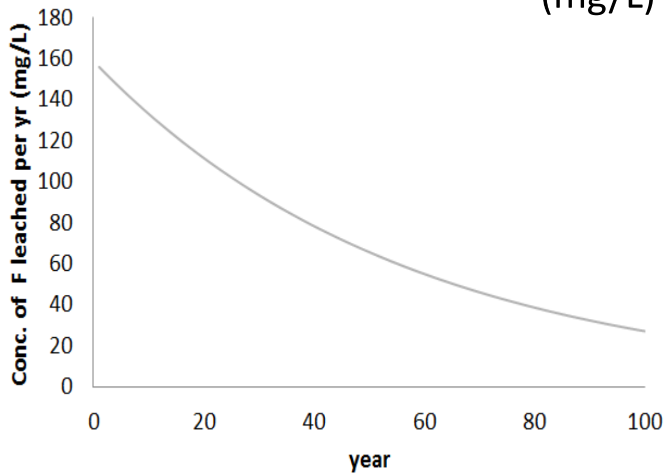
(Note) κ values provided by RIVM (95% upper confidence level)

Component	n	Average
F	6	0.22±0.14
Ni	37	0.29±0.05
Zn	41	0.28±0.05
As	44	0.03±0.05
Cd	37	0.50±0.10

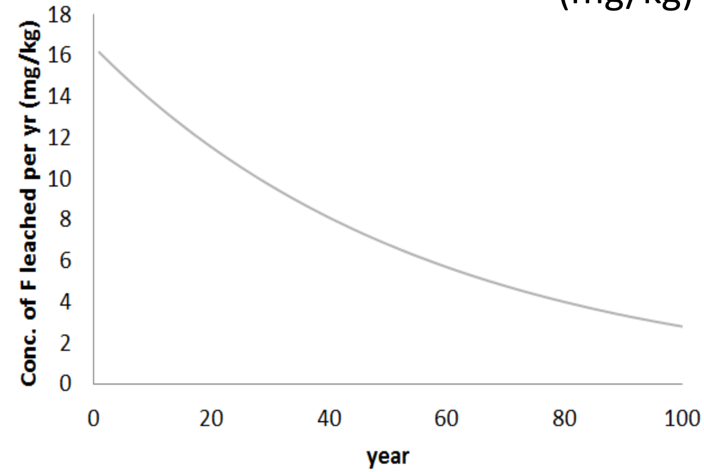
Component	n	Average
Cu	90	0.28±0.03
Cr	82	0.18±0.03
Hg	5	0.05±0.03
Pb	52	0.27±0.06

Long-term prediction results

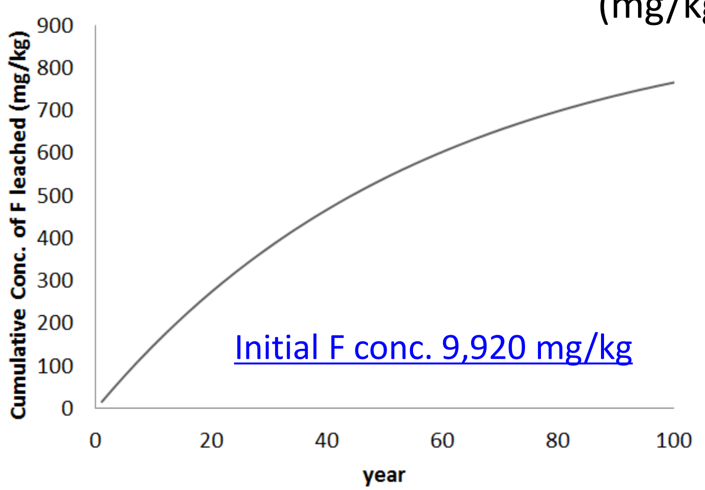
- F conc. in slag leachate with time (mg/L)



- F conc. leached from slag with time (mg/kg)



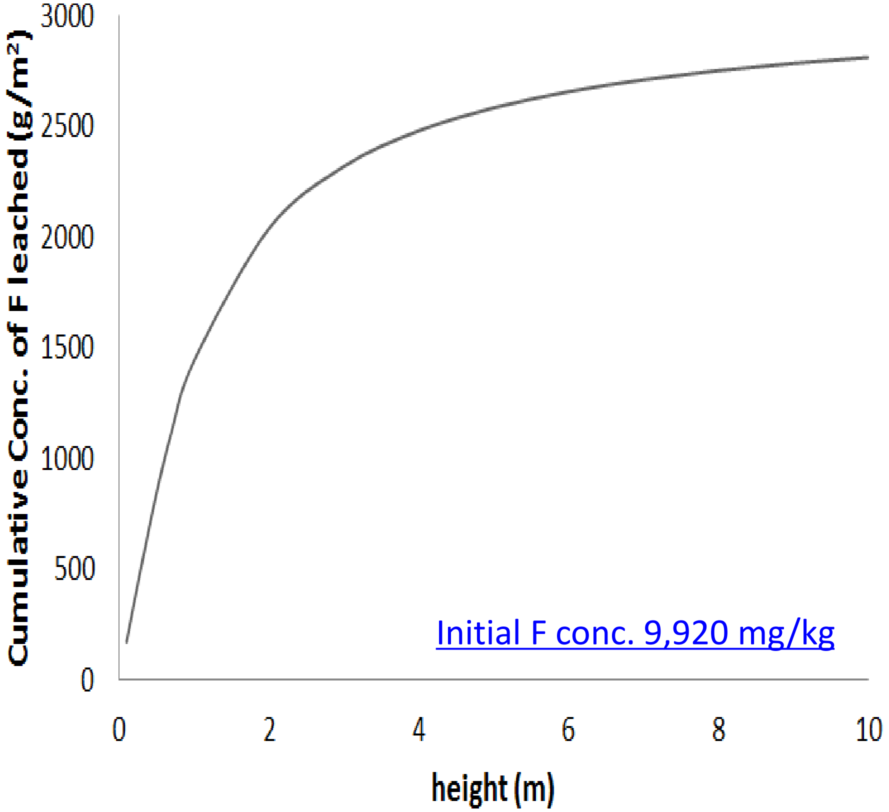
- Cumulative F conc. leached from slag (mg/kg)



☞ Cumulative conc. leached from slag (mg/kg)

In case of 1 m fill	F	**Ni**	**Zn**	**As**	**Cd**	**Cu**	**Pb**
	767	0.84	4.52	0.79	0.13	0.69	1.25

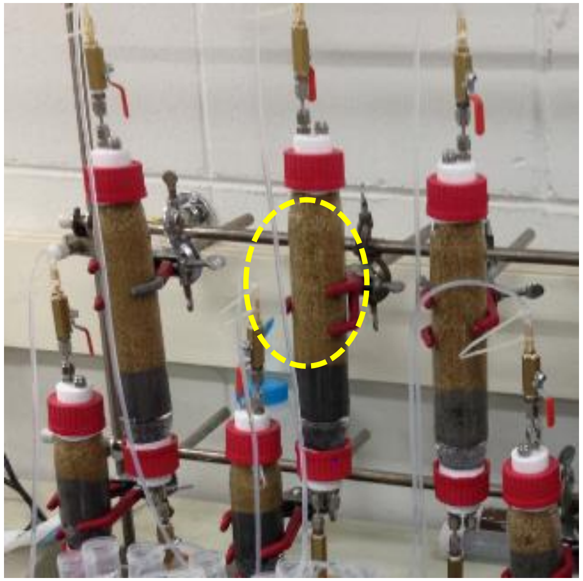
- 100-year accumulation of F conc. leached from slag-applied site (g/m²) depending on fill depth



Fill depth (m)	Cumulative conc. leached for 100 years (g/m²)
0.1	174
0.3	521
0.5	844
0.7	1,120
1	1,441
2	2,038
3	2,319
4	2,480
5	2,584
6	2,657
7	2,711
8	2,752
9	2,785
10	2,812

Impact on soil environment

- Potential impacts by leachates on soil beneath the slag layer was simulated.



- Slag to soil ratio, 1:9
- Column size: Ø4.5 × 36 cm = 572.6 cm^3
- Pore Volume: 198 ~ 201.4 cm^3
- Flow rate: 0.2 mL/min
- Simulated period: ca. 100 years (L/S ratio, 30)

☞ Soil characteristics

pH	TOC (%)	Sand (%)	Silt (%)	Clay (%)	Texture
6.27	1.50	15.2	48.8	36.0	Silty clay loam

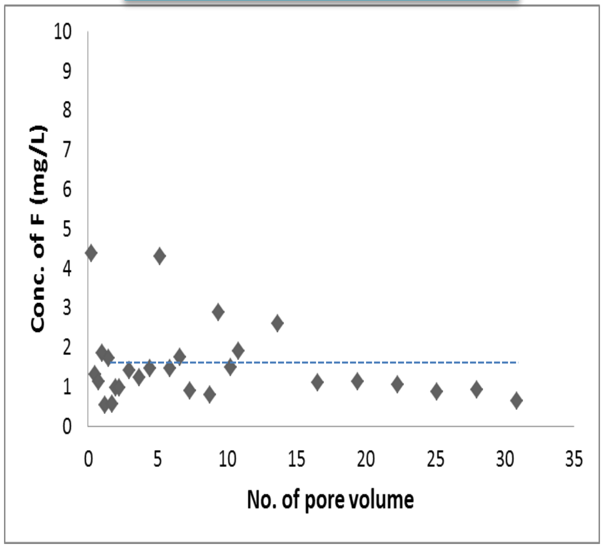
- Accumulation in soil beneath the slag

(unit: mg/kg)

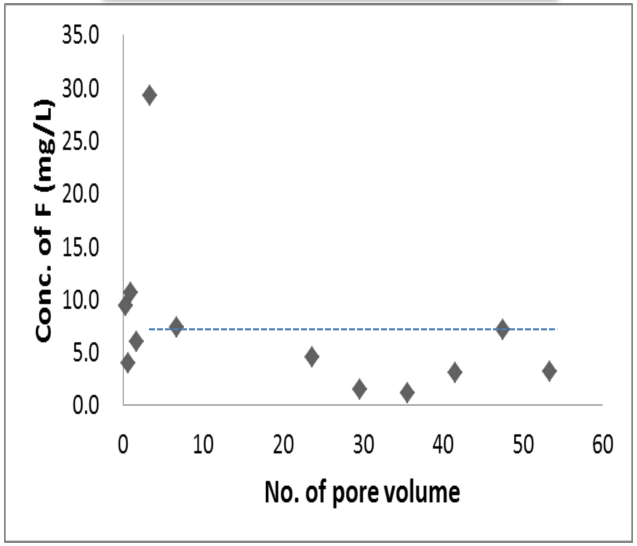
Sample	**F**	Ni	Zn	As	Cd	Cu	Cr^{6+}	Hg	Pb
Original soil	**235**	27.5	134	8.06	0.610	22.1	ND	0.05	14.5
Slag leachate-affected soil	**355**	30.0	153	8.42	0.810	24.2	ND	ND	16.3

- Change in F concentration in leachates

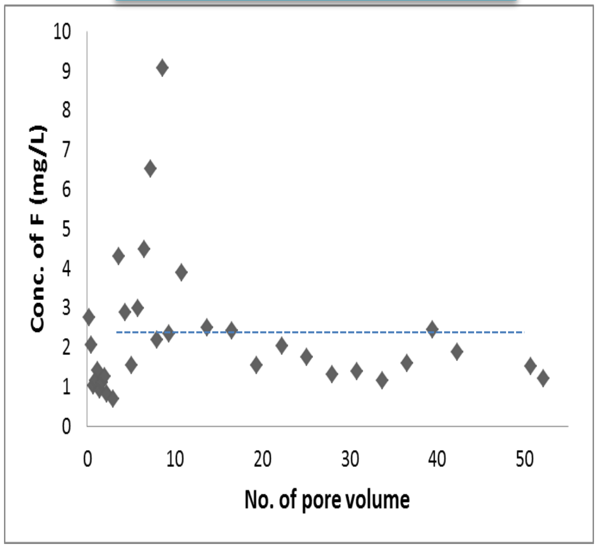
Soil-only layer leachate



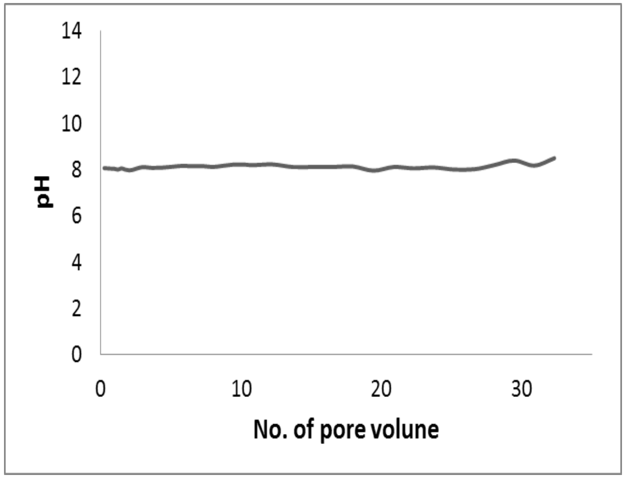
Slag-only layer leachate



Slag-soil layer leachate



- pH change in slag-soil layer leachate



✓ Original slag pH 13.4
✓ Original soil pH 6.27
✓ Slag leachate-affected soil pH 8.14

☞ Change in free CaO content
- original slag 4.27%
- after leaching 0.76% (slag pH decreased to 11.8)

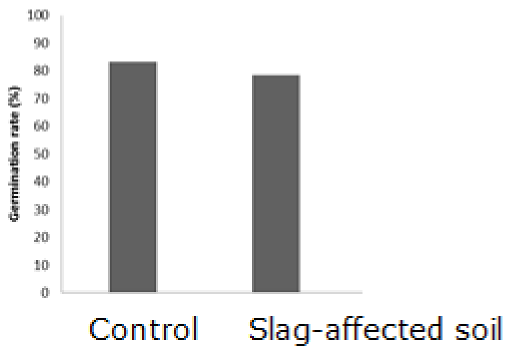
Impact on soil biota

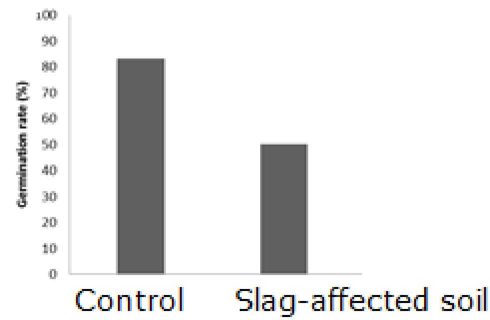
- Plant toxicity

	Procedure
Seed	*Spinapis alba* (Mustard), *Solanum lycopersicum* (Tomato)
Soil	30 g with water holding capacity
Period	12 days
Light Cycle	16/8 (L/D)
Temperature	23°C

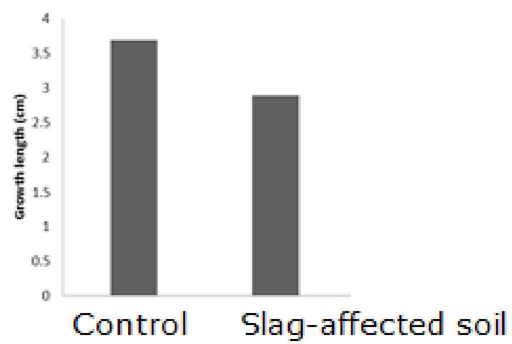
Spinapis alba (Mustard)

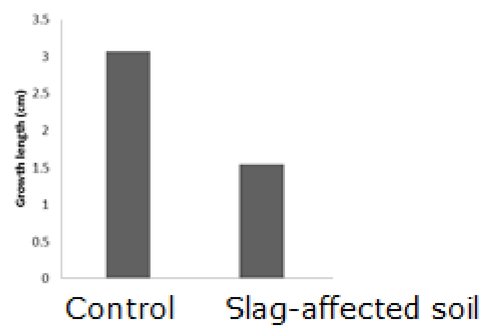
Solanum lycopersicum (Tomato)





Germination rate

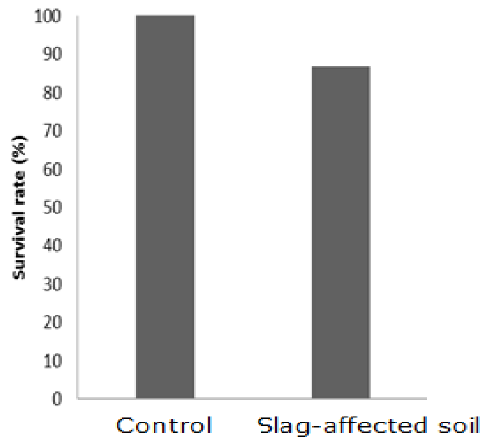




Grow length

- Earthworm toxicity

	Procedure
Species	*Eisenia foetida* (redworm)
Soil	100 g
Period	28 days
Light Cycle	16/8 (L/D)
Temperature	23°C



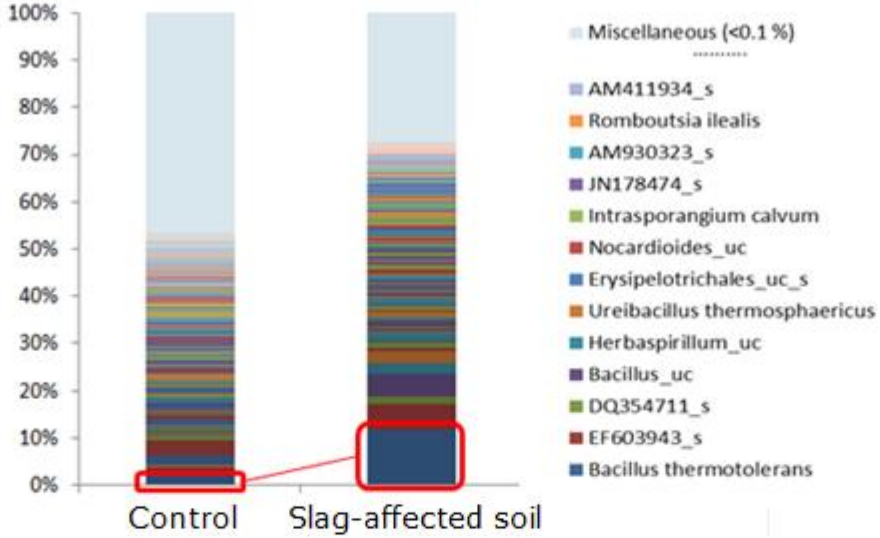
Survival rate

- Soil microbial toxicity: Enzyme activity test

Sample	Acid phosphatase (μg/g-soil)	Dehydrogenase (μg/g-soil)
Original soil	50.26	0.27
Slag leachate-affected soil	23.10	0.13

☞ Soil microbes seem to be affected the most.

- Change in soil microflora: Pyrosequencing (metagenomic analysis)



- ✓ Among the top 10 species, only 3 species remained.
- ✓ *Bacillus thermotolerans*: 2.2% → 11.6%
- ✓ Structure of microbial community changed.

  → What about "function"?

- Microbial diversity

Sample	Shannon Index[1)]	Simpson Index[2)]	OTUs[3)]
Original soil	6.769	0.002	2,092
Slag leachate-affected soil	5.753	0.012	1,361

1) Higher Shannon Index, higher microbial diversity
2) Lower Simpson Index, higher microbial diversity
3) Higher OTU (Operational Taxonomic Unit), higher microbial diversity

Summary

- Heavy metals and fluoride were rarely leached from the BOF slag tested in this study when determined by various leaching test methods. Also, total concentrations of heavy metals determined by *aqua regia* digestion met the Korean soil standards.

- However, fluoride concentration exceeded its Korean soil standard. Five-step sequential extraction data showed that most fluoride was present as non/less-labile forms. XRD and XPS analyses show the presence of fluoride-bearing minerals such as fluorite and cuspidine.

- Long-term prediction of leaching assuming percolation-controlled scenario indicates that less than 8% of total fluoride may leach from the slag for 100 years when 1-m fill was applied. Leaching of heavy metals for the same period was negligible.

- Tiered toxicity tests with the soil affected by the leachate from the BOF slag tested (i.e., simulated for 100 years) suggest the possibility of adverse effects on soil biota, especially on soil microflora. The reason may not be attributed to the compounds leached from the BOF slag, but to the alkaline pH of the leachate, which needs to be further verified.

Thank You for Attention !!!

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Balance Between Science & Technology

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