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Formation and dissolution of hexavalent Cr in Cr-containing steelmaking slag

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1 INTRODUCTION

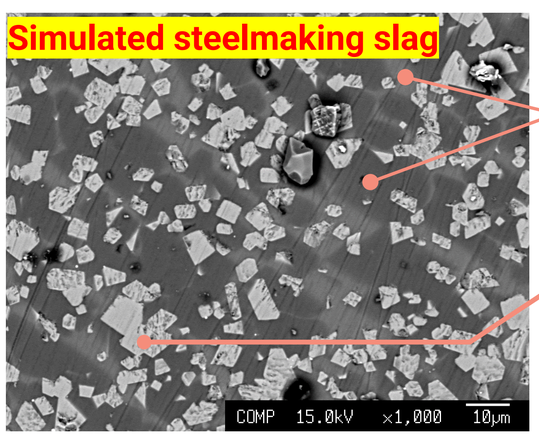
Raw materials → Electric furnace → Secondary refining

Some slag contains Cr.

EF slag
2.9Mt (fy2021)[1)]

Dissolution of Cr(VI) must be inhibited.

Road(40%), Civil(35%)[1)]



Ca,Mg,Fe silicate phase (containing 0.5~1mass%Cr_2O_3)

Main Cr-containing phase, $MgCr_2O_4$ (Cr(III))

Key points:
1. Suppressing Cr(VI) generation
   → Thermodynamic condition of Cr(VI)/Cr(III)
2. Inhibiting dissolution and dispersion
   → Control dissolution behavior

2 METHODS

①Isothermal TG & DSC (Thermodynamic study)

Decomposition Reaction:

$MgCrO_4(s) = 1/2MgO(s) + 1/2MgCr_2O_4(s) + 3/4O_2(g)$
($MgCrO_4$: Cr(VI), $MgCr_2O_4$: Cr(III))

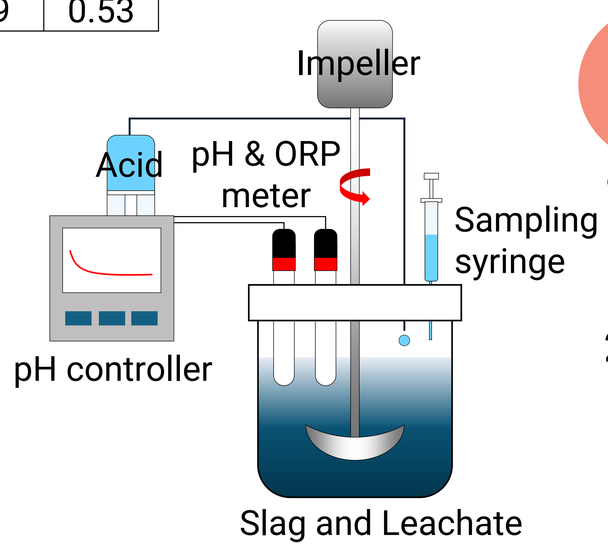
Sample: $MgCrO_4$ obtained by decomposing $MgCrO_4 \cdot 5H_2O$ (<105μm)

Atmosphere: O_2 1atm

②Dissolution test (Elution control)

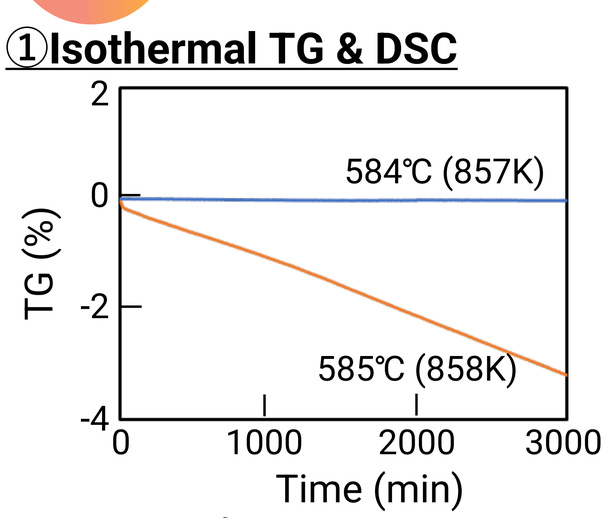
Slag (mass%)						
CaO	SiO_2	FeO	Cr_2O_3	MgO	bal.	C/S
18.4	34.6	4.3	19.2	13.6	9.9	0.53

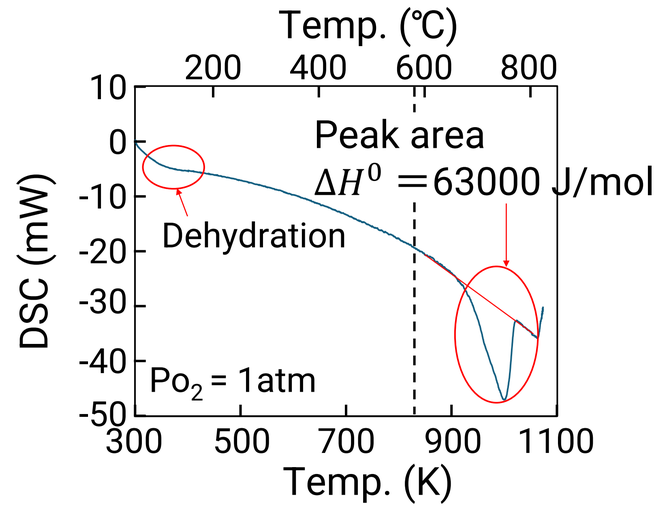
Sample	Actual Cr-containing slag	
	Weight	2.5g
	Powder diameter	＜75μm
Solution	Distilled water	
	Volume	1000 mL
pH		Uncontrolled, 6, 4, 3 (controlled by 1M-HCl)
Temperature		R.T. (293～298K)
Stirring		Impeller 200 r.p.m.
Atmosphere		Air



3 RESULTS & DISCUSSION

①Isothermal TG & DSC





$\Delta G = \Delta G^0 + RT\ln K = 0$ at equilibrium condition

$$\Delta G^0 = -RT\ln K = -RT\ln \frac{a_{MgO}{}^{\frac{1}{2}} \cdot a_{MgCrO_4}{}^{\frac{1}{2}} \cdot Po_2{}^{\frac{3}{4}}}{a_{MgCrO_4}}$$

Assuming activity of solid equals 1, and P_{O2}=1 atm,

$$\Delta G^0 = -\frac{3}{4}RT\ln Po_2 = 0 = \Delta H^0 - T\Delta S^0$$

At equilibrium temperature, $T_{eq.}$,

$$\Delta S^0 = \Delta H^0 / T_{eq.}$$

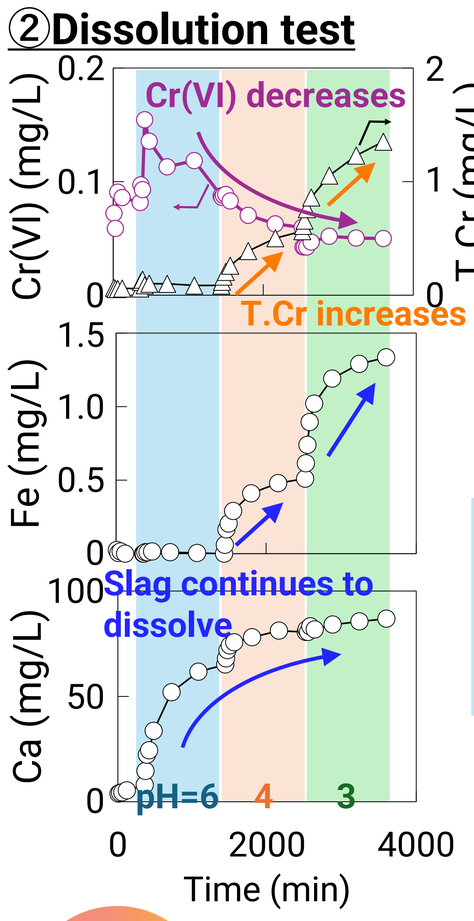
Representing enthalpy change of decomposition by DSC method,

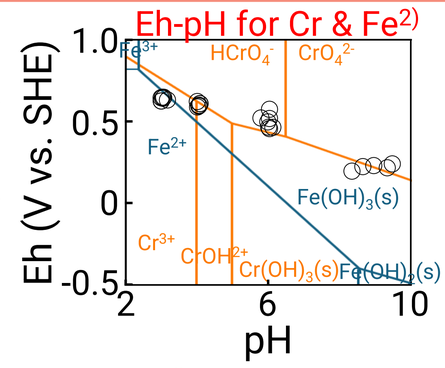
$$\Delta H^0 = 63000, \Delta S^0 = 73.4, \Delta G^0 = 63000 - 73.4T\ (J/mol)$$

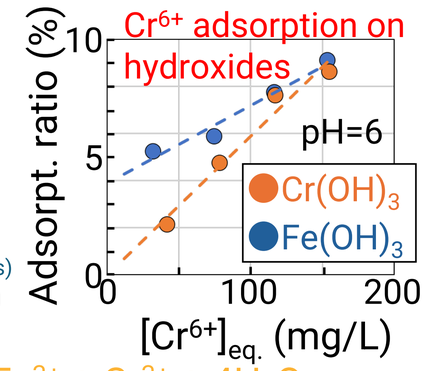
Air atmosphere (P_{O2}=0.21atm) → Decomposition temperature=484℃

Quenching slag from 484℃ or higher to suppress formation of $MgCrO_4$(Cr(VI))

②Dissolution test



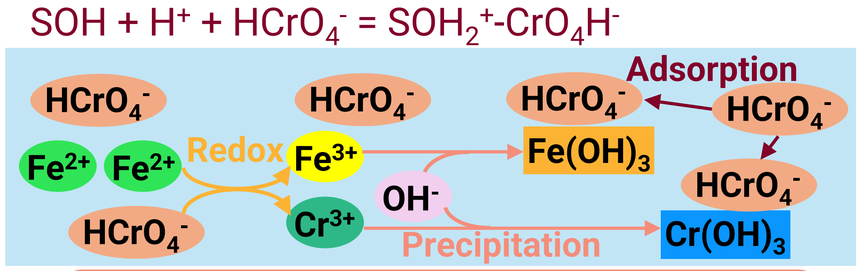




$7H^+ + 3Fe^{2+} + HCrO_4^- = 3Fe^{3+} + Cr^{3+} + 4H_2O$

$Fe^{3+} + 3OH^- = Fe(OH)_3\downarrow$, $Cr^{3+} + 3OH^- = Cr(OH)_3\downarrow$

$SOH + H^+ + HCrO_4^- = SOH_2^+\text{-}CrO_4H^-$



With Fe dissolution, Cr dissolution can be suppressed under environmental conditions.

4 CONCLUSION

1. **Gibbs free energy change of following reaction are determined.**
   $MgCrO_4(s) = 1/2MgO(s) + 1/2MgCrO_4(s) + 3/4O_2(g)$
   $\Delta G^0 = 63000 - 73.4T\ (J/mol)$
2. **Dissolution of Cr(VI) from slag is suppressed by dissolution of components in slag.**

REFERENCES

1. Nippon slag association, https://www.slg.jp/e/
2. M. Pourbaix, Atlas of Electrochemical Equilibria in Aqueous Solution, Natl Assn of Corrosion Engineers, Houston, 1974.