Trial of Capillary Refining by Porous CaO with Molten Slag

Toshihiro Tanaka & Masanori Suzuki
Osaka University, Japan
Surface of materials:
- High reactivity,
- Adsorption,
- Wetting
- Surface tension etc.

Application of the above properties to development of materials, materials processing, recycling etc.

Porous materials
Highly Efficient Usage of Solid CaO

"Efficient " means:

1. More rapid transfer of P or S than diffusion in solid CaO
   lumps / particle / powder

2. Even inside of solid CaO should be used for reaction.
   It is difficult to recycle slag containing unreacted CaO.

The reduction of the total amount of slag generation.
Solid CaO Flux

without CaF₂

Highly Efficient Usage of Solid CaO
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.

Capillary tubes
(Pores between CaO grains etc.)

New Refining Procedure using Capillary in Solid CaO

Dephosphorization and Desulfurization

CaCO₃ → CaO + CO₂

5 μm
Capillary Penetration

Capillary Penetration

Spontaneously
(without Energy)

To remove Impurities from Liquid into Solid phase

"Capillary Refining"

e.g. Absorption of Water in “Tissue paper”
**Capillary Refining** for De-P & De-S in Liq. Fe

**Capillary Tubes**

**Diffusion** in solid is very slow, but penetration is rapid!!

**Porous CaO**

**Molten Slag**

Penetration of Molten Slag into Solid CaO

with $P_2O_5$ & CaS
“Capillary Refining”

1. How to prepare Porous CaO??

2. How to prepare Molten Slag??

Diagram showing the interaction between Porous CaO, Molten Slag, and Liquid Fe.
Outline:

[1]. *How to make porous solid CaO*

[2]. *Examples of Capillary Refining for Desulfurization of Liquid Fe*

[3]. *How to prepare Molten Slag at the interface between Solid CaO and Liquid Fe*
1. How to prepare Porous CaO?

From Ca(OH)$_2$

From mixture of CaCO$_3$+chloride

Hard-burning of CaCO$_3$ at 1200$^0$C

Soft-burning of CaCO$_3$ at 900$^0$C
Outline:

[1]. How to make porous solid CaO

[2]. Examples of Capillary Refining for Desulfurization of Liquid Fe

[3]. How to prepare Molten Slag at the interface between Solid CaO and Liquid Fe
"Capillary Refining" for De-S in Liq. Fe

Molten slag must be equilibrated with pure solid CaO phase.
"Capillary Refining" for De-S in Liq. Fe

Molten SiO_2-CaO-MgO -35%Al_2O_3 Slag

1450°C

Porous CaO

CaO after penetration of slag

Observation

Penetration

Surface of molten slag

Porous CaO

Forefront

Penetration of Molten Slag

Ca

5 micro-m

S exists at forefront

Mg

Al

Si
De-S by CaO with molten CaO-Al\(_2\)O\(_3\) slag
Outline:

[1]. How to make porous solid CaO

[2]. Examples of Capillary Refining for Desulfurization of Liquid Fe

Not good for industrial extension

[3]. How to prepare Molten Slag at the interface between Solid CaO and Liquid Fe
De-S by Immersion of Porous CaO coated with Al$_2$O$_3$
Solid CaO coated with Al₂O₃ powder

Dynamic Formation of Molten Slag Layer

SEM

Penetration

Surface of molten slag

Observation

CaO

Slag

Liq. Fe

Molten slag

Porous CaO

100μm

10μm

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Second International Slag Valorisation Symposium | Toshihiro Tanaka & Masanori Suzuki

28/04/2011
De-S by Porous CaO with Al\textsubscript{2}O\textsubscript{3} powder

Penetration of Molten Slag & Sulfur inside CaO
Outline:

[1]. How to make porous solid CaO

[2]. Examples of Capillary Refining for Desulfurization of Liquid Fe

[3]. How to prepare Molten Slag at the interface between Solid CaO and Liquid Fe

Thin Molten Slag Layer might be enough ???

How to make Thin Molten Slag Layer between Solid CaO and Liquid Fe
De-S by **Immersion of Porous CaO in liquid Fe containing Al**

*Fe-Csat-0.05mass%Al-0.1mass%S*
*1600°C*
*for 30min*
*Ar*
De-S by **Immersion of Porous CaO in liquid Fe containing Al**

- CaO penetration
- Surface of molten slag
- Observations
- Molten Slag Thin Layer: about 300 micron
- SEM images:
  - Ca: 46.6%
  - S: 46.8%
  - Al: 0.3%
  - O: 6.3%

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De-S by **Immersion of Porous CaO in liquid Fe containing Al**

**Observation**

Penetration of Molten Slag & Sulfur inside CaO

**Surface of molten slag**

**Thin Layer**: about 300 micron

**CaO**

**Molten Slag**

**10μm**

**100μm**

**10μm**
"Capillary Refining"

Porous Solid CaO

Thin layer of Molten Slag

\[
\alpha_{\text{CaO}} = \text{High Basicity}
\]

CaS Formation

Concentration of Sulfur

\[
[S\text{ in Slag (CaO)}] > [S\text{ in Fe}]
\]

Chemical Potential of Sulfur

\[
\mu_{S\text{ in Slag(CaO)}} > \mu_{S\text{ in Fe}}
\]

Gradient of Chemical Potential of Sulfur Can be kept.
"Green Metallurgy"
for Sustainable Resource Circulation

Capillary Refining

Recycling of Slag

Porous CaO

Molten Slag

Liq.Fe

Interface

Solid CaO

Penetration of Molten Slag Into Solid CaO

P₂O₅? CaS?

Capillary Tubes

Porous Slag
used for filter, insulator etc.
"Capillary Refining" for Dephosphorization in Hot Metals

Oxidation liq. Fe

→ FeO + P₂O₅

→ Molten Slag

→ Penetration into Inner wall of CaO

Oxygen

CaO Crucible

Graphite Crucible

Liquid Fe-P C saturated Alloy
“Capillary Refining” for Dephosphorization

Oxygen

Solid CaO

Molten Slag

Solid CaO

Molten Slag

Liq. Fe

Interface

About 1mm

Penetration of Molten Slag

Penetration region of Molten Slag

SEM

Solid CaO

FeO Base Slag

Forefront of Penetration

20μm

P

P2O5
Coexisting with Pure solid CaO
Keep activity of CaO to be unity.
Rotary Kiln

$\text{Fe}_2\text{O}_3$ or $\text{Al}_2\text{O}_3$

Porous CaO

Composite of Porous CaO coated with $\text{FeO}_x$ or $\text{Al}_2\text{O}_3$

Blowing Gas ($\text{O}_2$, $\text{Ar}$) with Composite CaO

Hot Metal
\[ L = \left( r \cdot \frac{\sigma}{\eta} \right) \cdot t \]^{1/2}

**L**: Penetration Distance at time \( t \)

**\( r \)**: Radius of Capillary

**\( \sigma \) & **\( \eta \)**: Surface Tension & Viscosity of Molten Slag

**Calculation of Penetration Flow Rate**

**Solid**

**Molten Slag**

**Diffusion in solid is slow.**

High Surface Tension & Low Viscosity of Liquid → High Capillary Flow Rate

\( r = 1 \times 10^{-6} \text{m} \)

\( \sigma/\eta = 10 \)

\( \sigma/\eta = 5 \)

\( \gamma/\eta = 1 \)
"Capillary Refining"

- Slow Diffusion
- Reaction products stop reactions.
- Rapid penetration
- Good Wettability
- Continuous reactions

Diagram:
- Dense Solid CaO
- Porous CaO
- Molten Slag
- Liquid Fe