

# ***Trial of Capillary Refining by Porous $\text{CaO}$ with Molten Slag***

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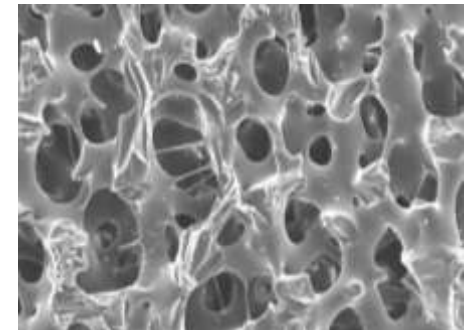
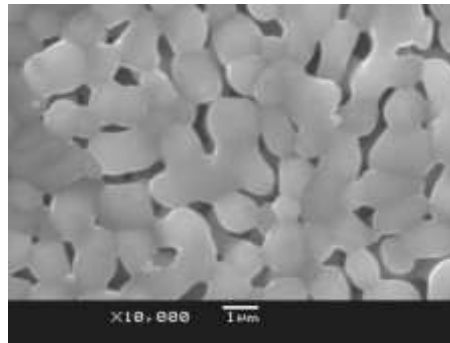
# Laboratory on Surface Science in Metallurgy

**Surface of materials :**  
**High reactivity,**  
**Adsorption,**  
**Wetting**  
**Surface tension etc.**

***Div. Materials &  
Manufacturing  
Science,  
Osaka University***

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

## **Porous materials**

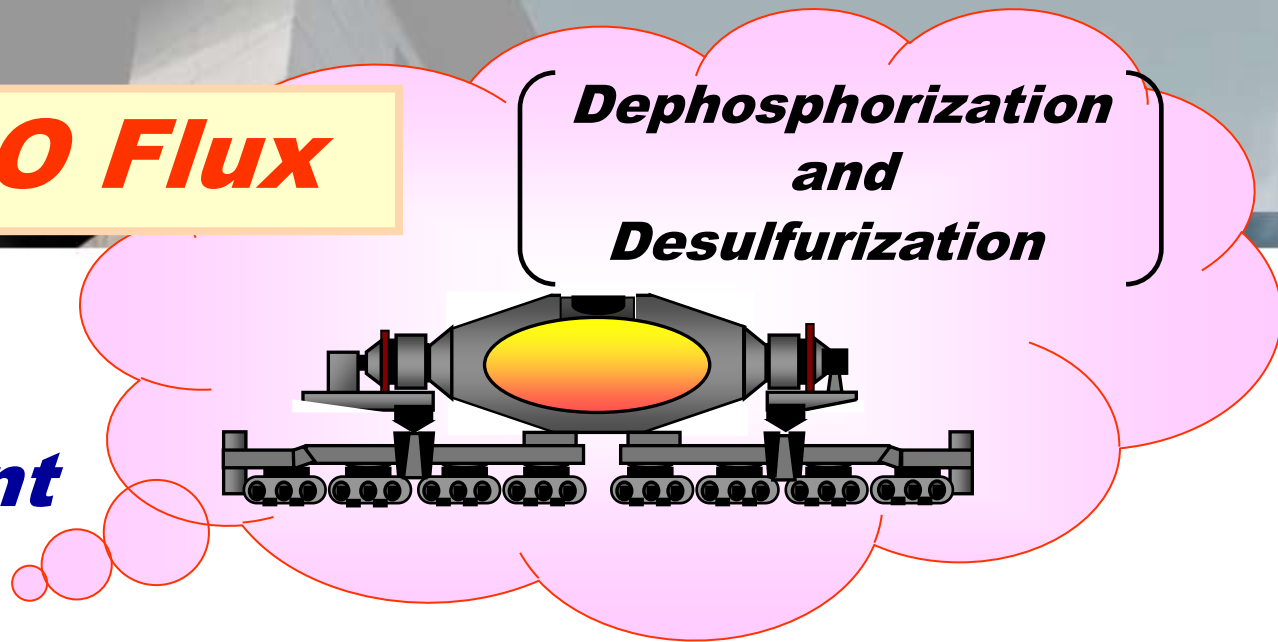


# ***Solid CaO Flux***

*without CaF<sub>2</sub>*



***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**.

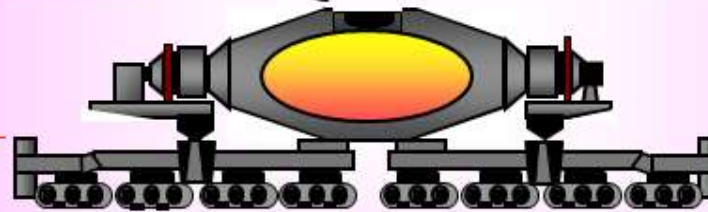


# Solid CaO Flux

without  $\text{CaF}_2$

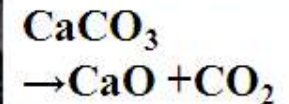
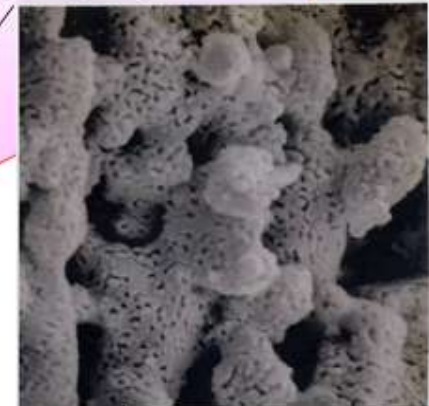
Highly Efficient  
Usage  
of Solid CaO  
...

Dephosphorization  
and  
Desulfurization



Capillary tubes  
(Pores between  
CaO grains etc.)

Solid CaO  
powders, lumps



5 μm

New Refining Procedure  
using Capillary in Solid CaO

# Capillary Penetration

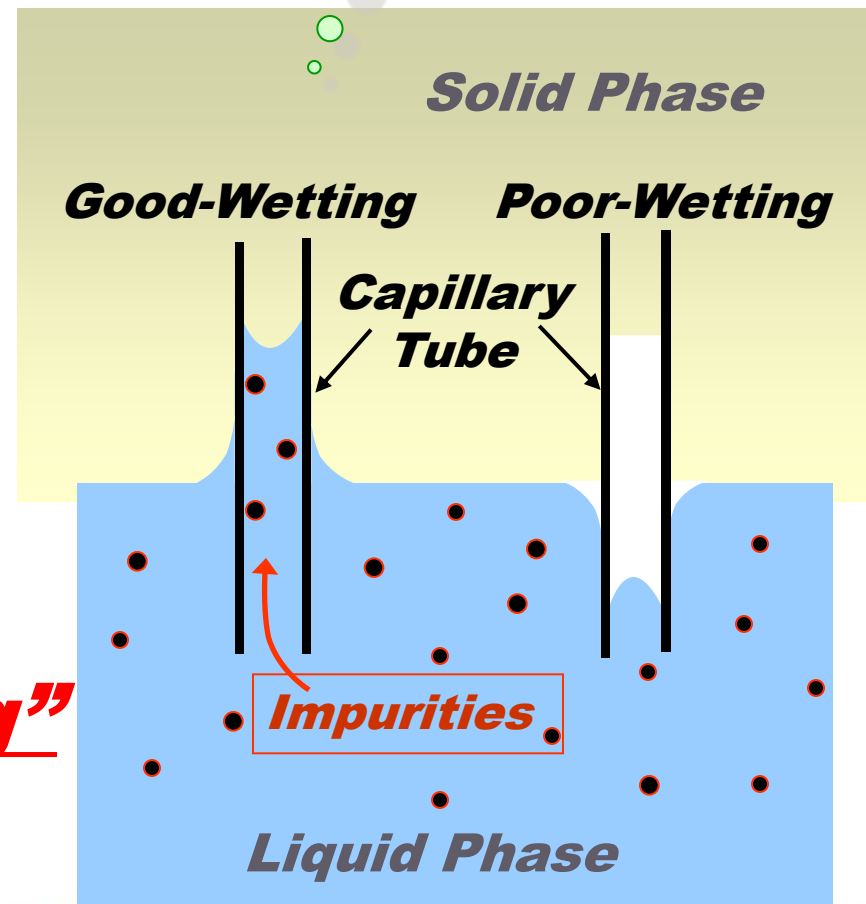
e.g. Absorption of Water in "Tissue paper"

## Capillary Penetration

**Spontaneously  
(without Energy)**

To remove Impurities from  
Liquid into Solid phase

**"Capillary Refining"**



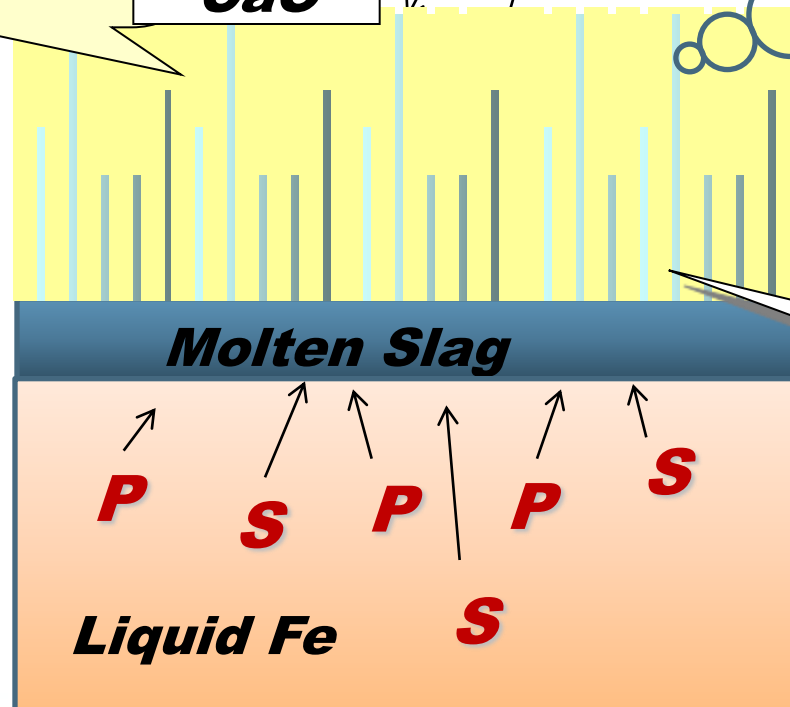
# **“Capillary Refining”** for *De-P & De-S* in *Liq. Fe*



**Porous  
CaO**

**Capillary  
Tubes**

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



**with  $P_2O_5$   
& CaS**

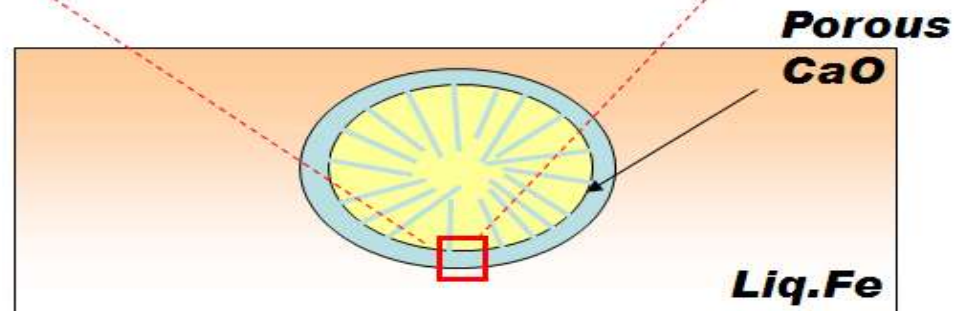
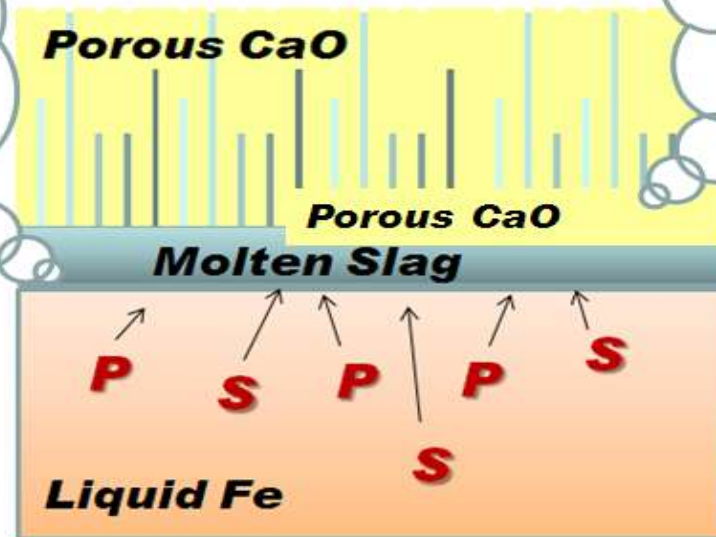
**Penetration of  
Molten Slag  
into Solid CaO**

# ***“Capillary Refining”***

## **“Capillary Refining”**

**2. How to  
prepare  
Molten  
Slag ??**

**1. How to  
prepare  
Porous  
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*



# Porous Solid CaO

[1]

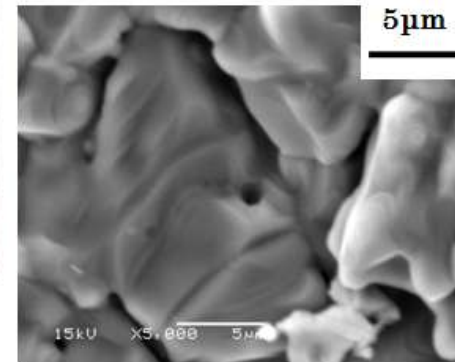
**1. How to  
prepare  
Porous  
CaO ??**



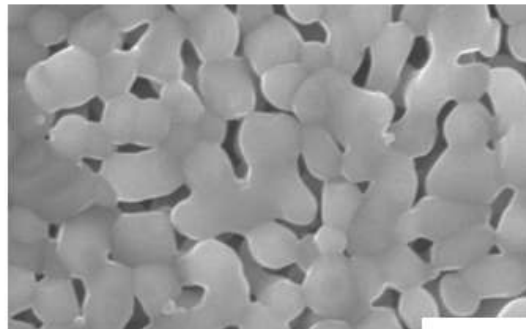
3μm

Soft-burning of  
 $\text{CaCO}_3$  at  $900^\circ\text{C}$

Hard-burning of  
 $\text{CaCO}_3$  at  $1200^\circ\text{C}$

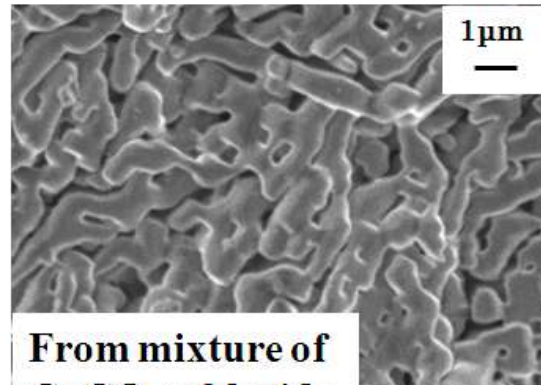


5μm



1μm

From  $\text{Ca}(\text{OH})_2$



1μm

From mixture of  
 $\text{CaCO}_3$ +chloride

# Outline :

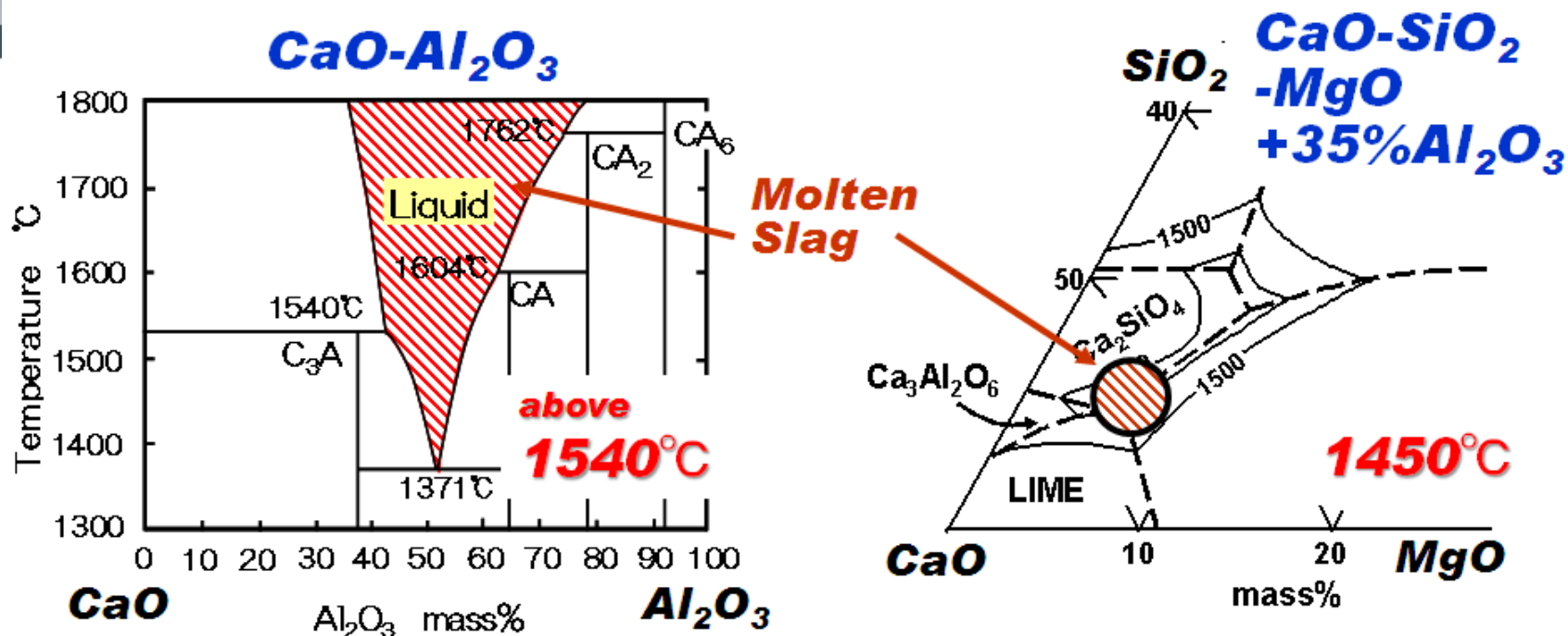
[1]. *How to make porous solid CaO*

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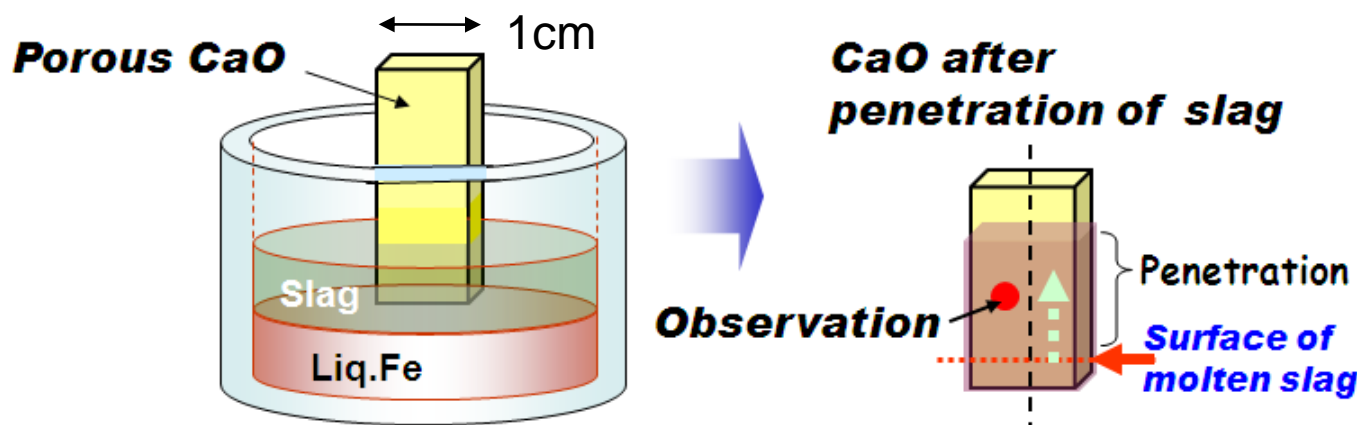
[3]. *How to prepare Molten Slag  
at the interface  
between Solid CaO and Liquid Fe*

[2]

# “Capillary Refining” for De-S in Liq. Fe

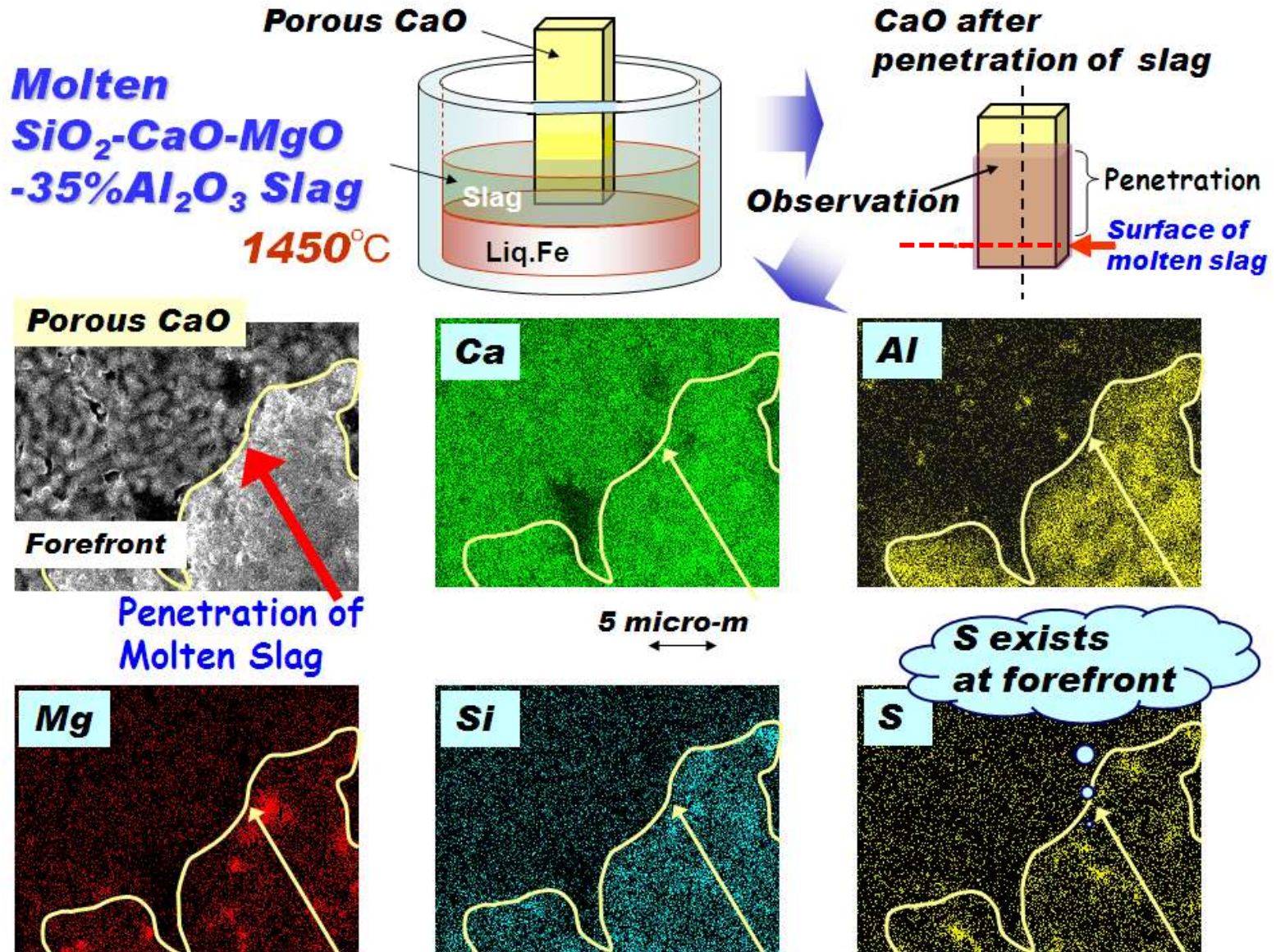


**Molten slag must be equilibrated with pure solid  $\text{CaO}$  phase.**



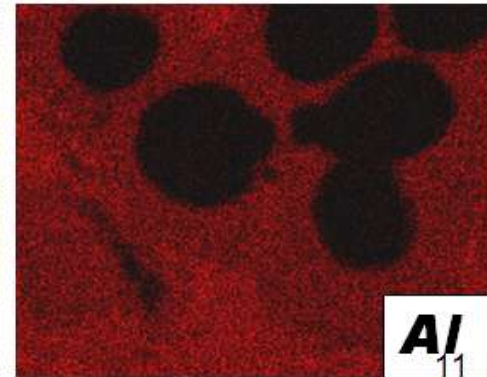
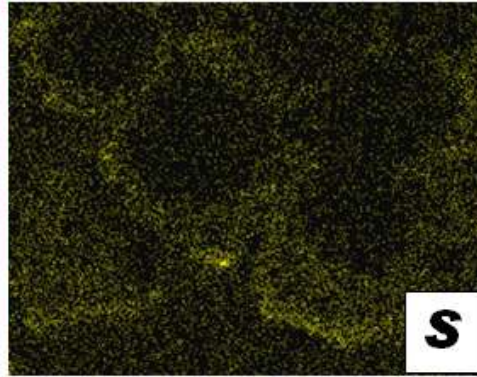
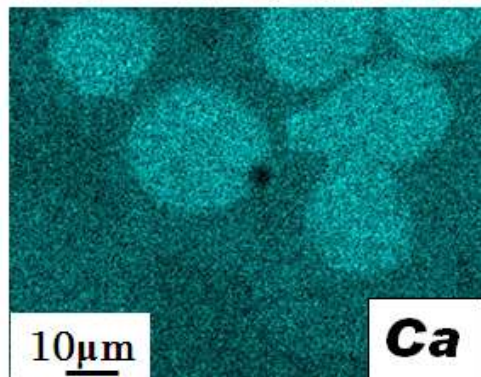
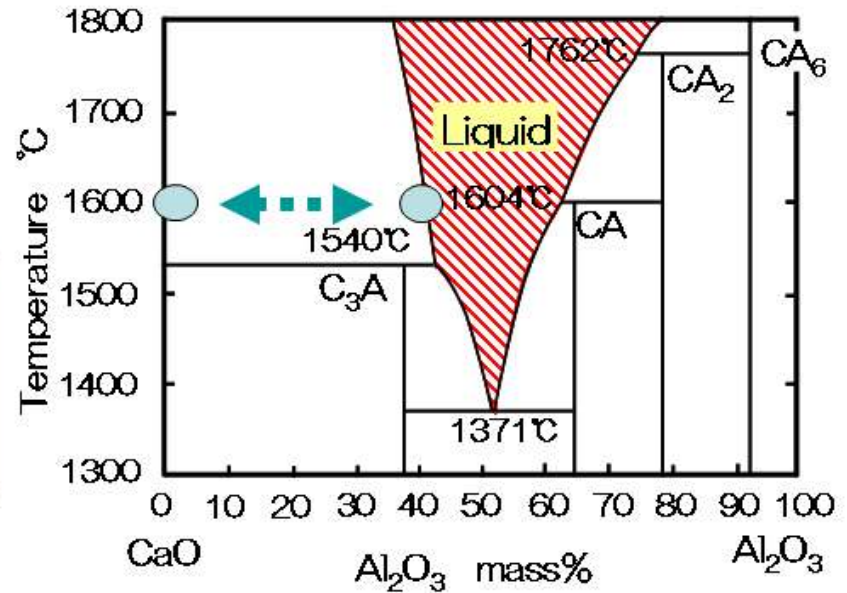
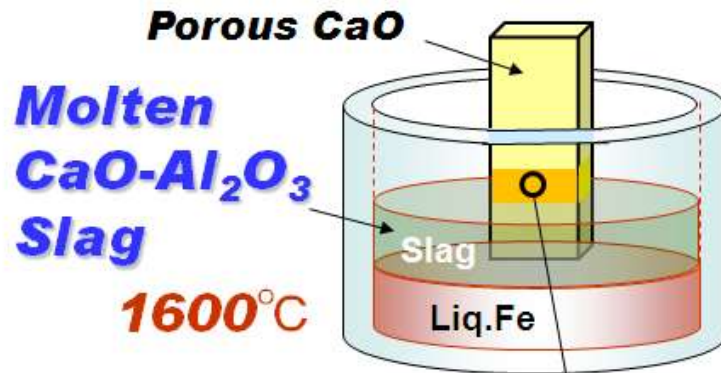


# **“Capillary Refining” for De-S in Liq. Fe**





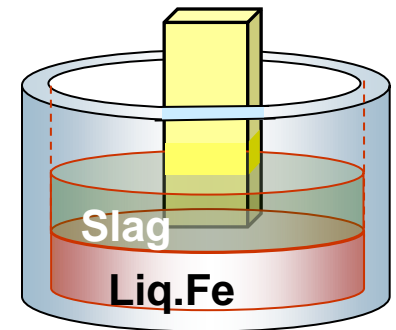
# De-S by CaO with molten CaO-Al<sub>2</sub>O<sub>3</sub> slag



# Outline :

- [1]. *How to make porous solid CaO*
- [2]. *Examples of Capillary Refining for Desulfurization of Liquid Fe*

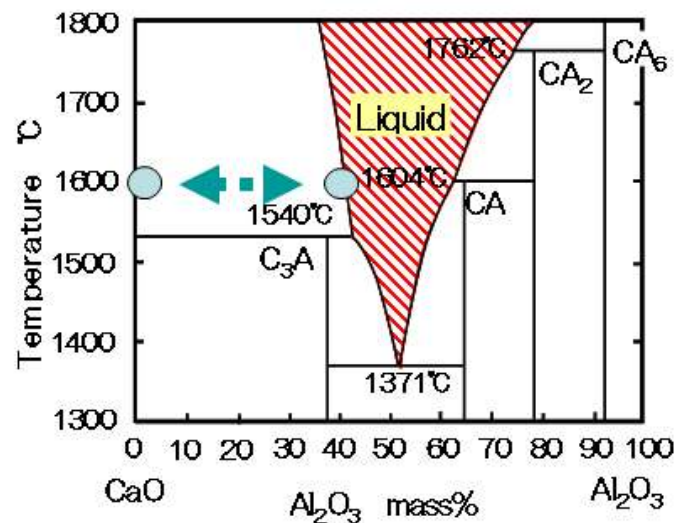
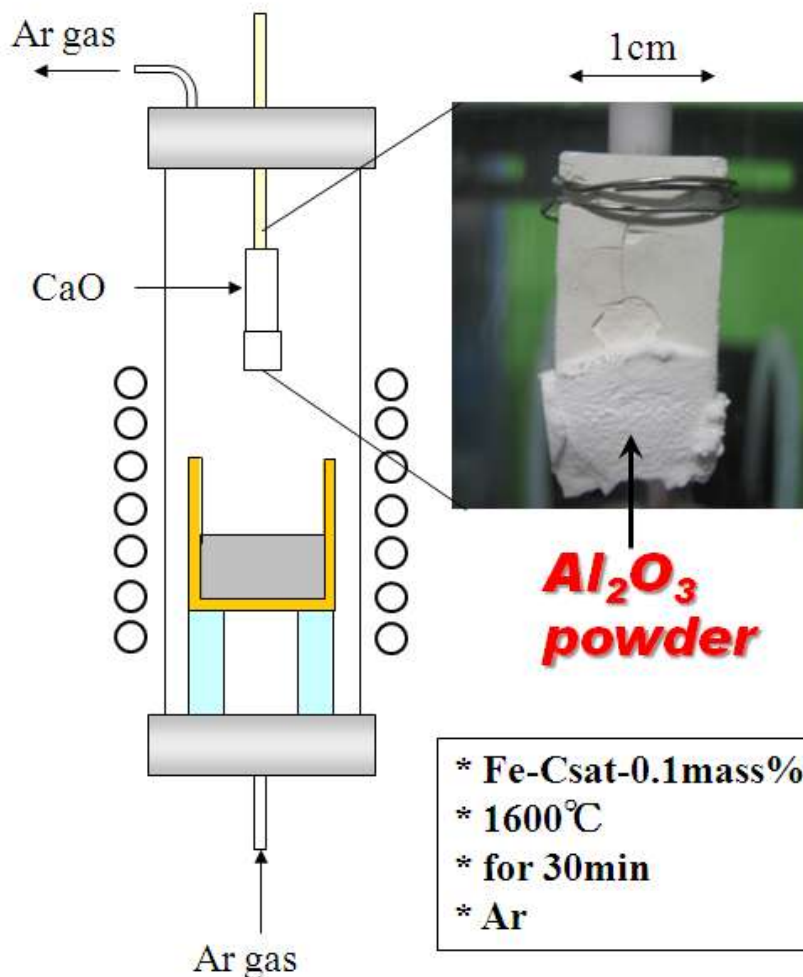
Not good for  
industrial extension



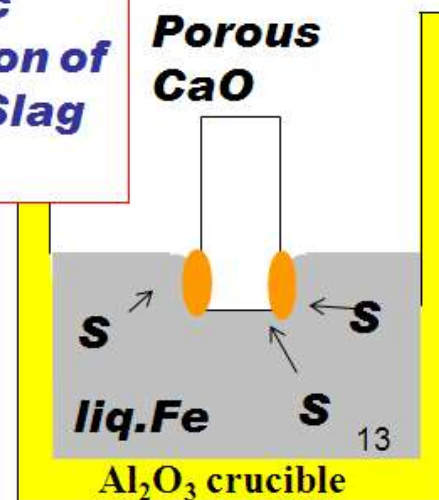
- ➔ [3]. *How to prepare Molten Slag at the interface between Solid CaO and Liquid Fe*

[3]

# De-S by Immersion of Porous CaO coated with $\text{Al}_2\text{O}_3$



**Dynamic Formation of Molten Slag Layer**

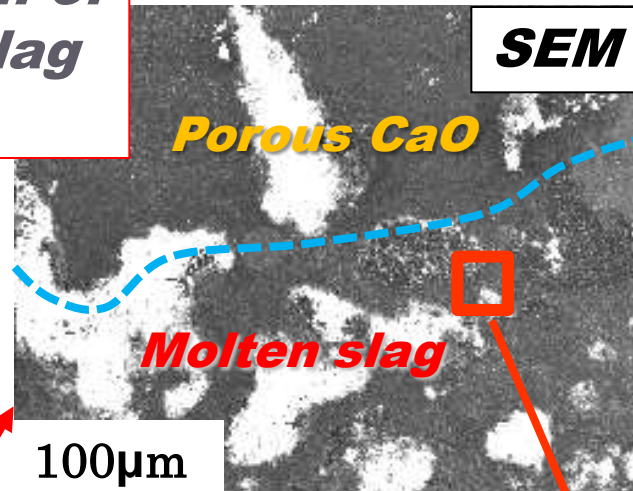




# ***Solid CaO coated with $Al_2O_3$ powder***



***Dynamic  
Formation of  
Molten Slag  
Layer***

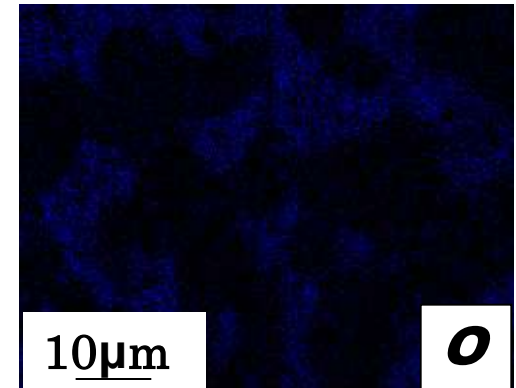


**SEM**

***Porous CaO***

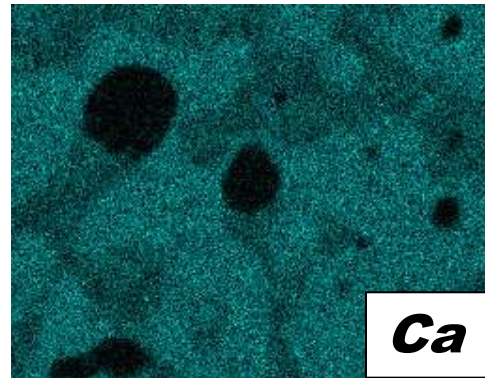
***Molten slag***

100µm

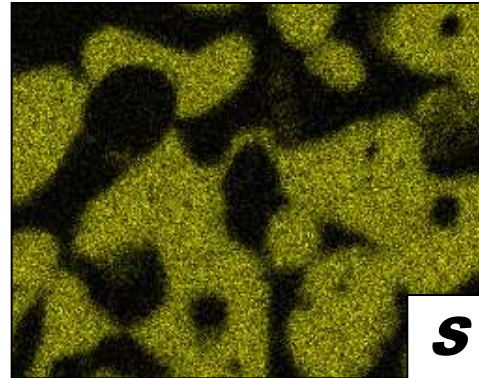


**O**

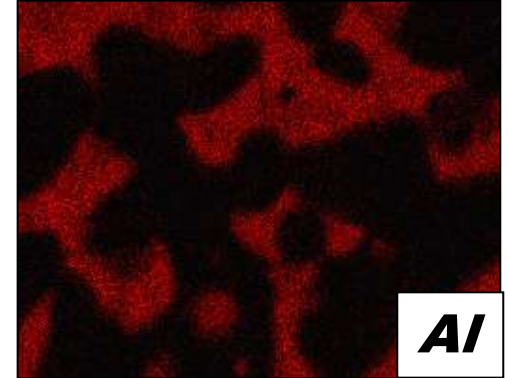
10µm



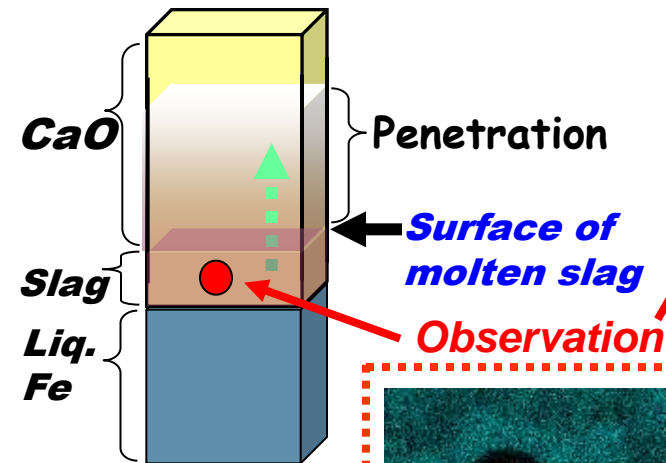
**Ca**



**S**

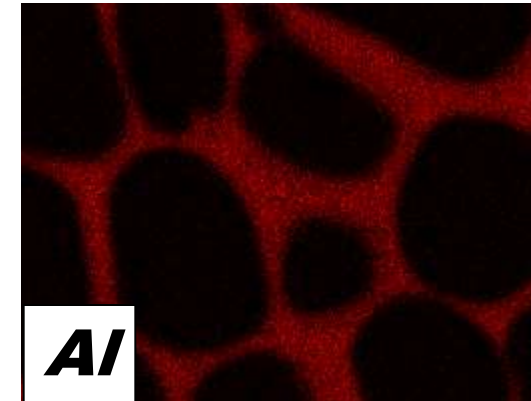
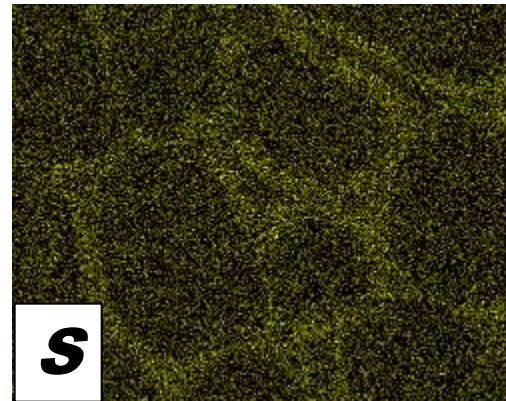
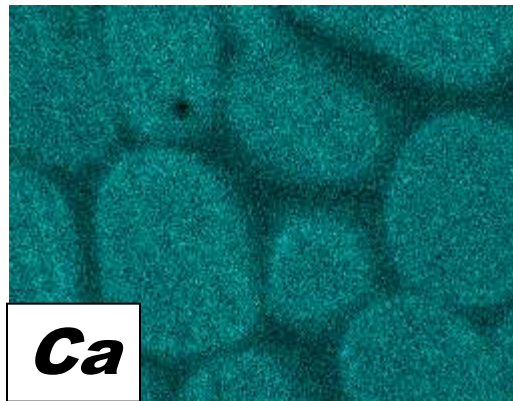
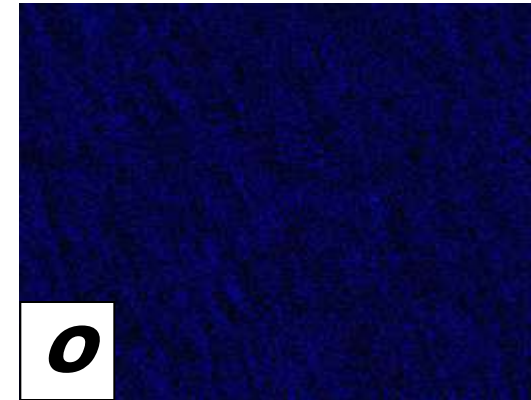
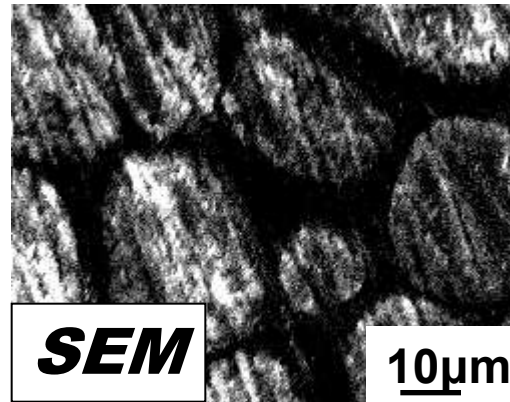
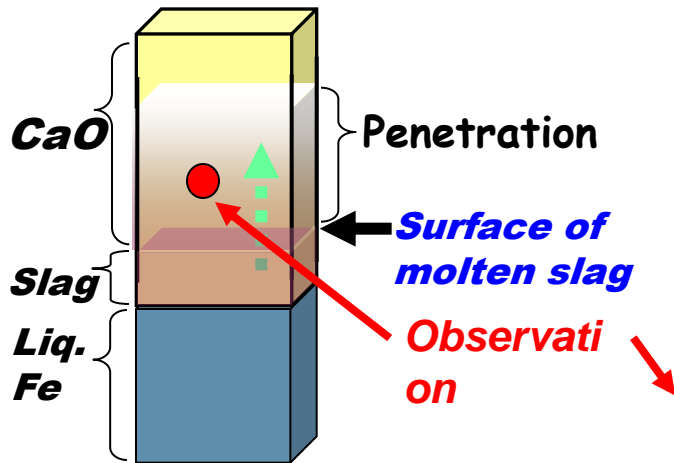


**Al**





# ***De-S by Porous CaO with $Al_2O_3$ powder***



**Penetration of Molten Slag & Sulfur inside CaO**

# Outline :

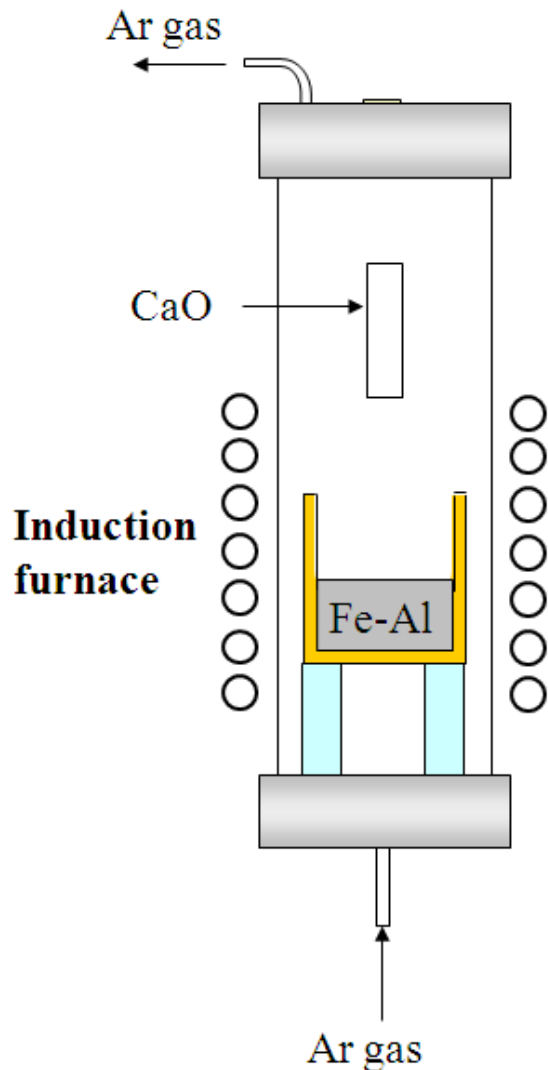
- [1]. *How to make porous solid CaO*
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for Desulfurization of Liquid Fe*
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at the interface  
between Solid CaO and Liquid Fe*

Thin Molten Slag Layer might be enough ???

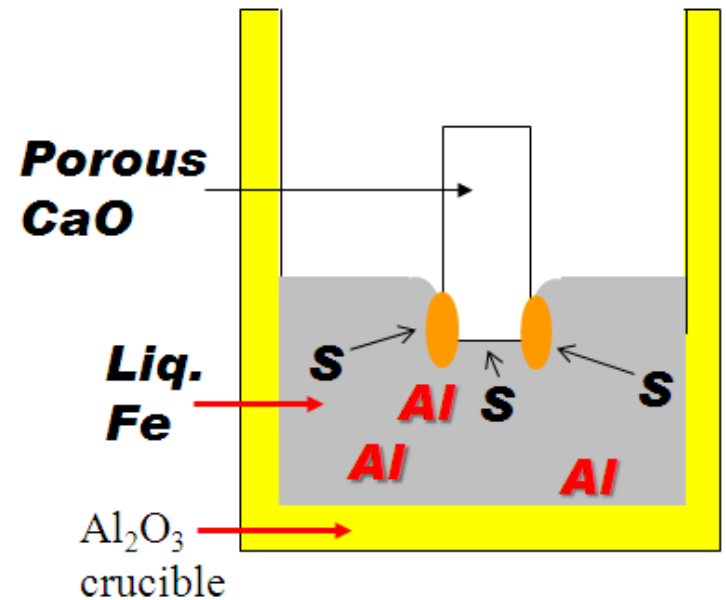


***How to make Thin Molten Slag Layer  
between Solid CaO and Liquid Fe***

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



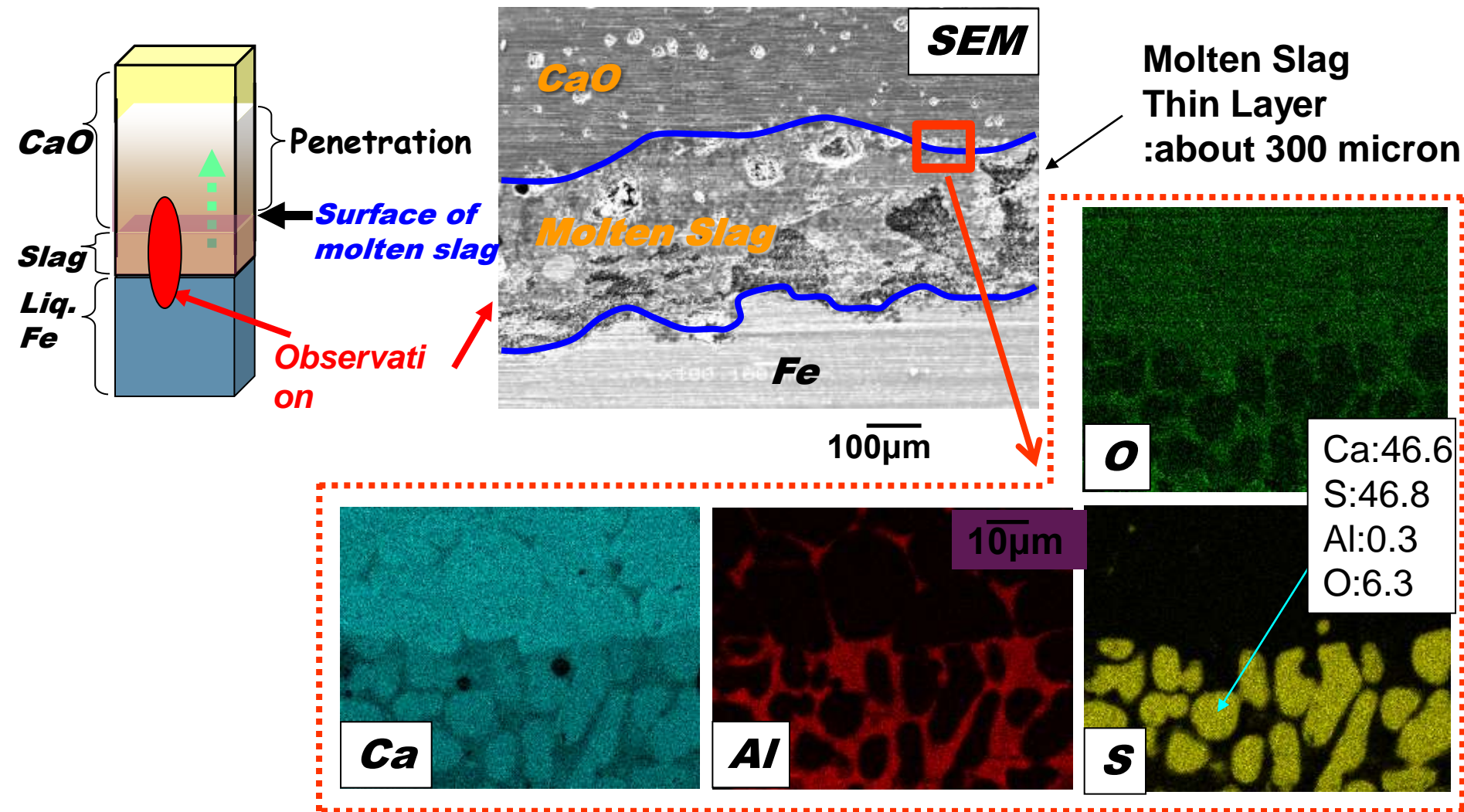
***Dynamic  
Formation of  
Molten Slag  
Layer***



- \* Fe-Csat-0.05mass%Al-0.1mass%S
- \* 1600°C
- \* for 30min
- \* Ar

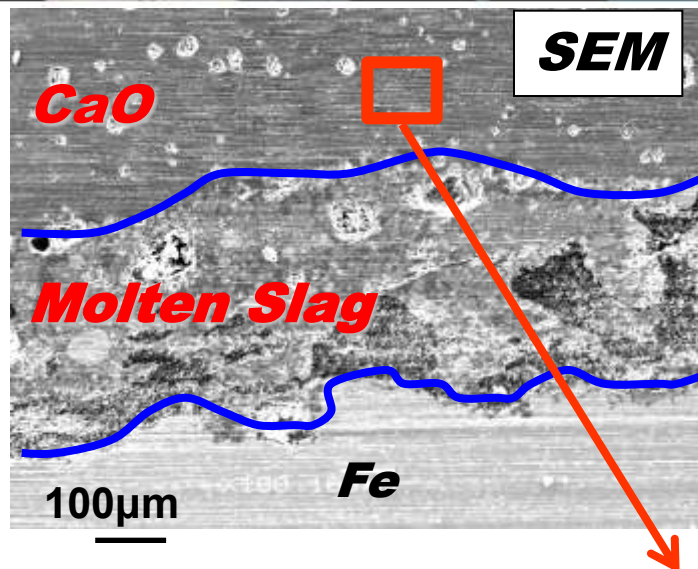
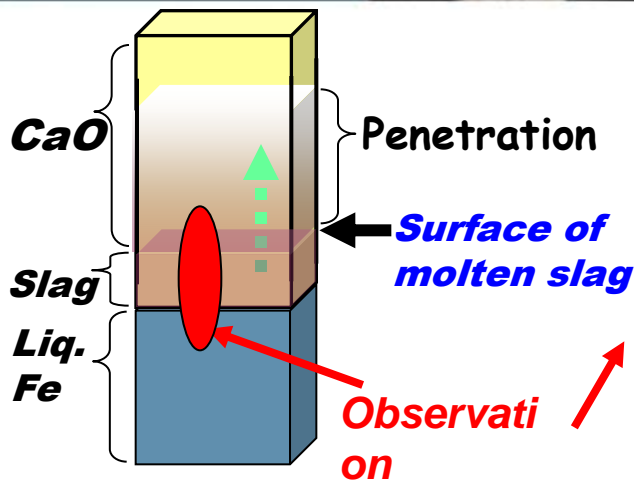


# De-S by *Immersion* of Porous $\text{CaO}$ in *liquid Fe* containing *Al*

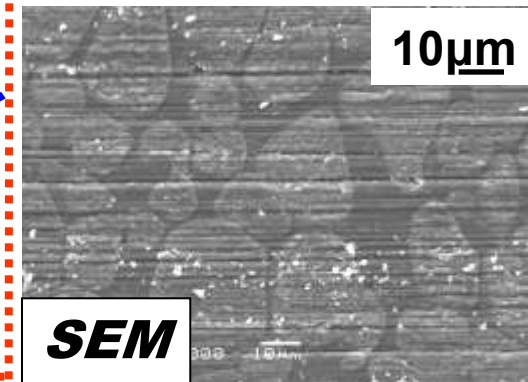




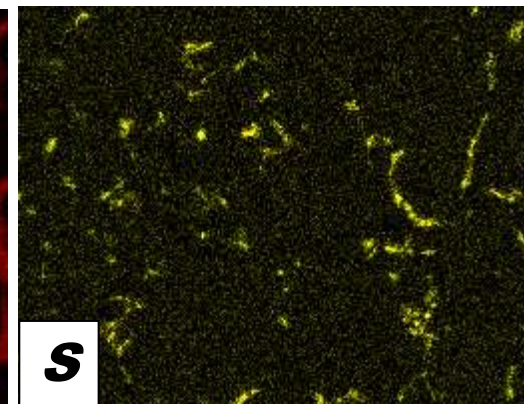
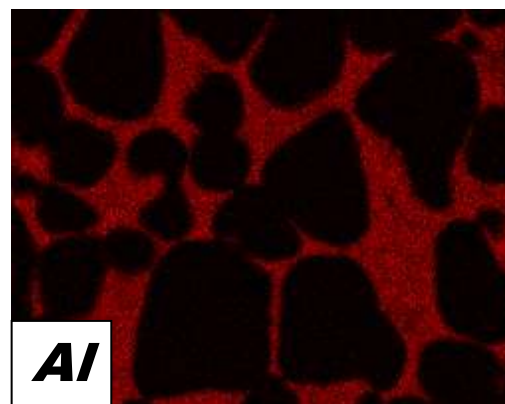
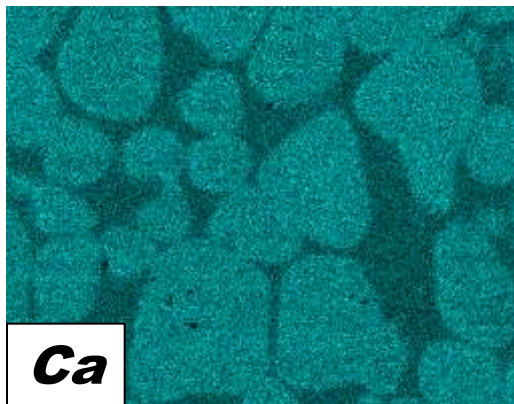
# *De-S by Immersion of Porous CaO in liquid Fe containing Al*



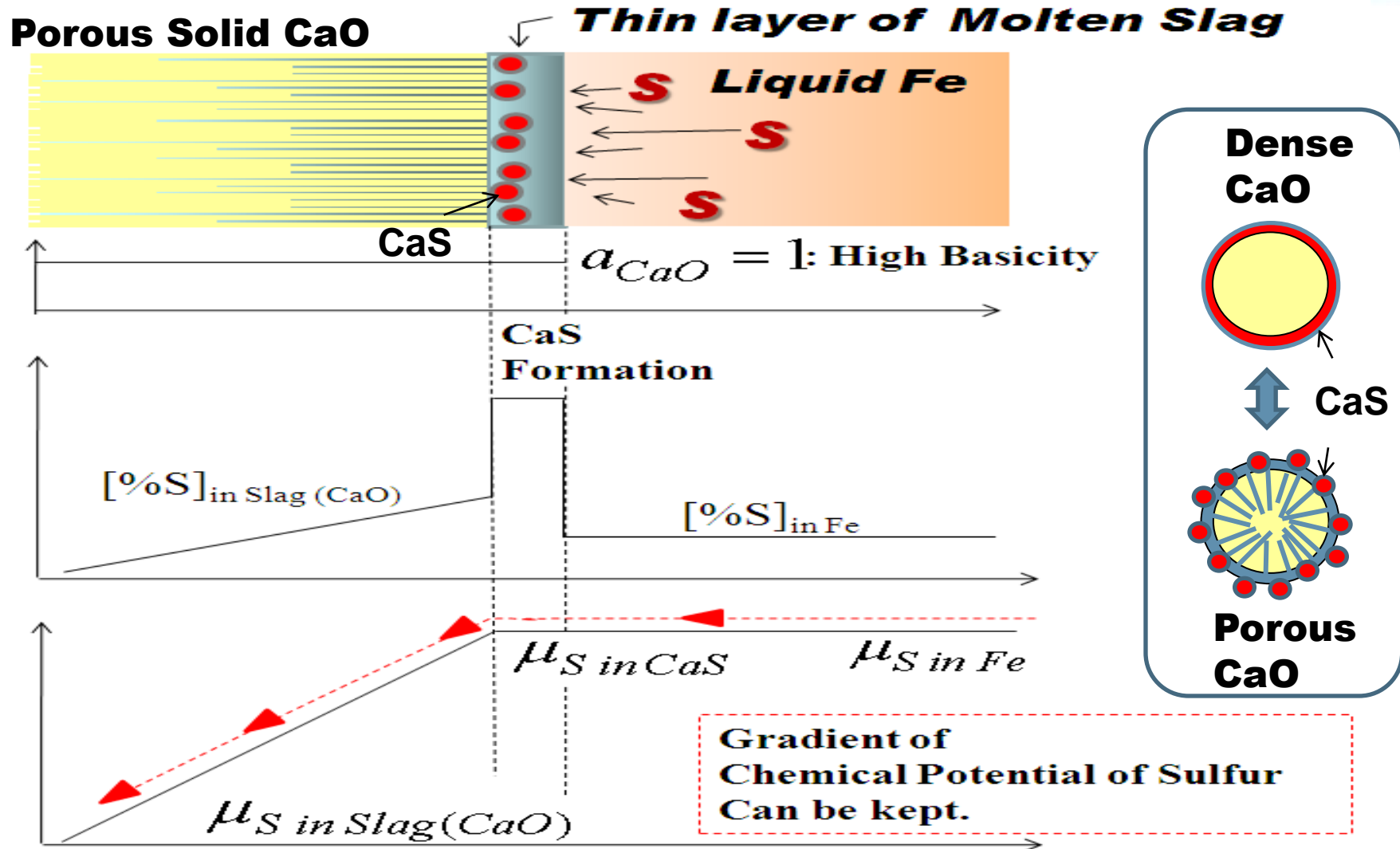
Molten Slag  
Thin Layer  
:about 300  
micron



Penetration of Molten Slag & Sulfur inside CaO



# “Capillary Refining”

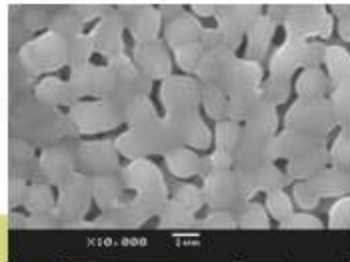


# “Green Metallurgy”

## for Sustainable Resource Circulation

### Capillary Refining

**Porous  
CaO**



**Capillary  
Tubes**

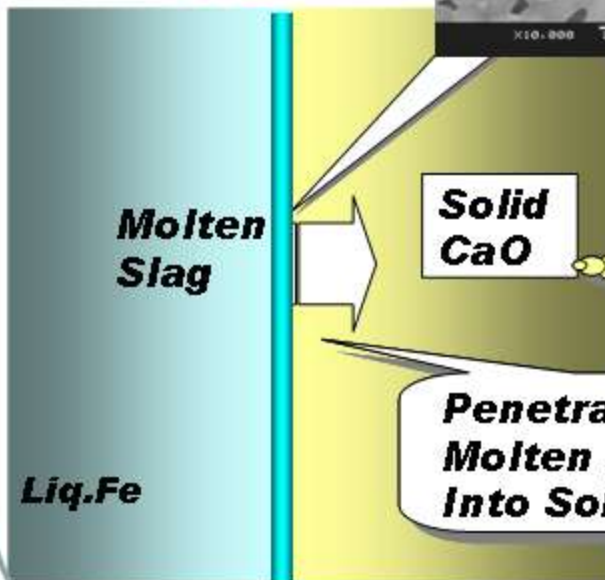
**Solid  
CaO**

**$P_2O_5$ ?**

**CaS?**

**Penetration of  
Molten Slag  
Into Solid CaO**

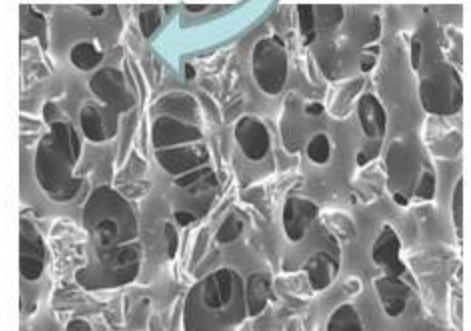
**Interface**



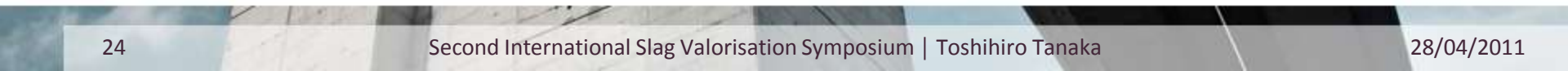
### Recycling of Slag



**Porous  
Slag**



**used for filter,  
insulator etc.**





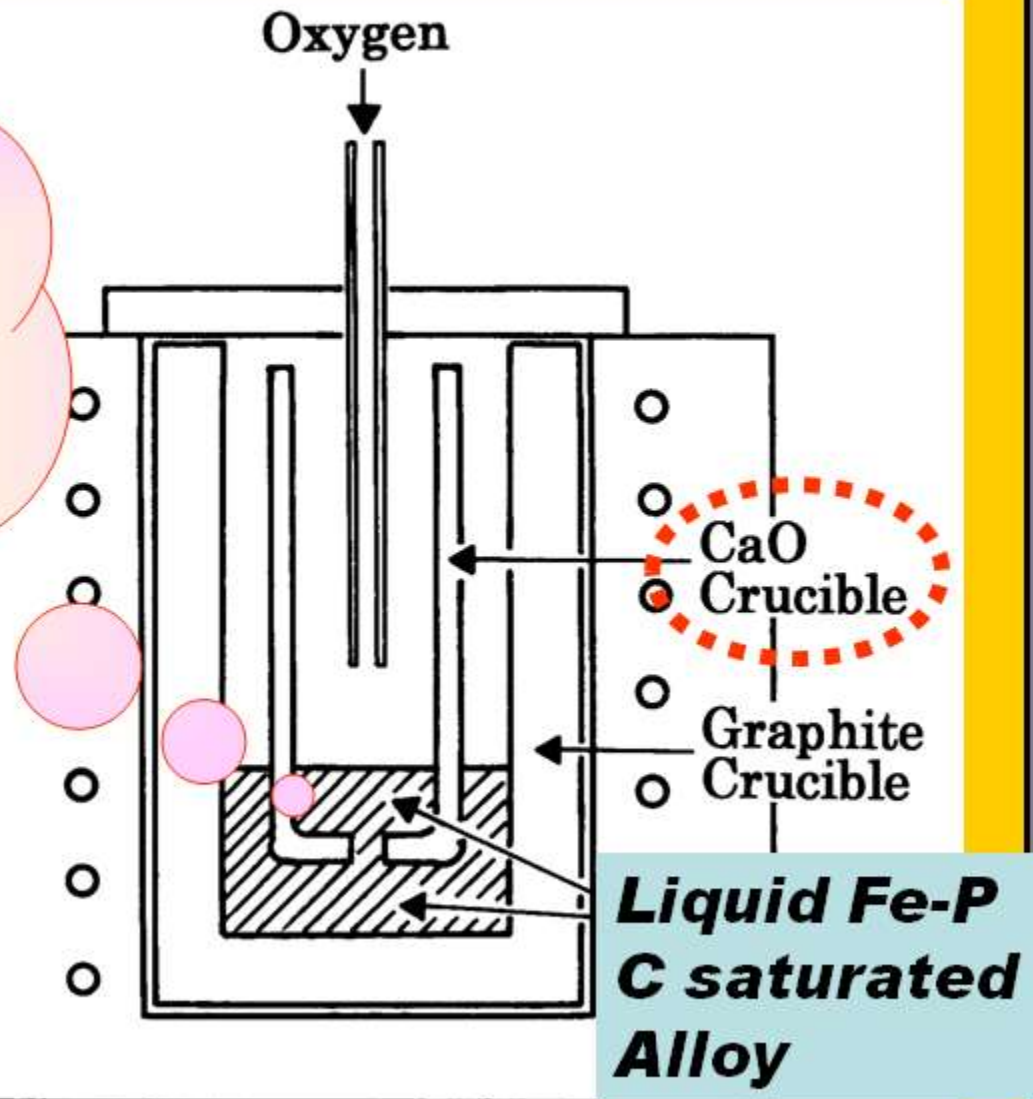
# **“Capillary Refining” for Dephosphorization in Hot Metals**

Oxidation liq. Fe

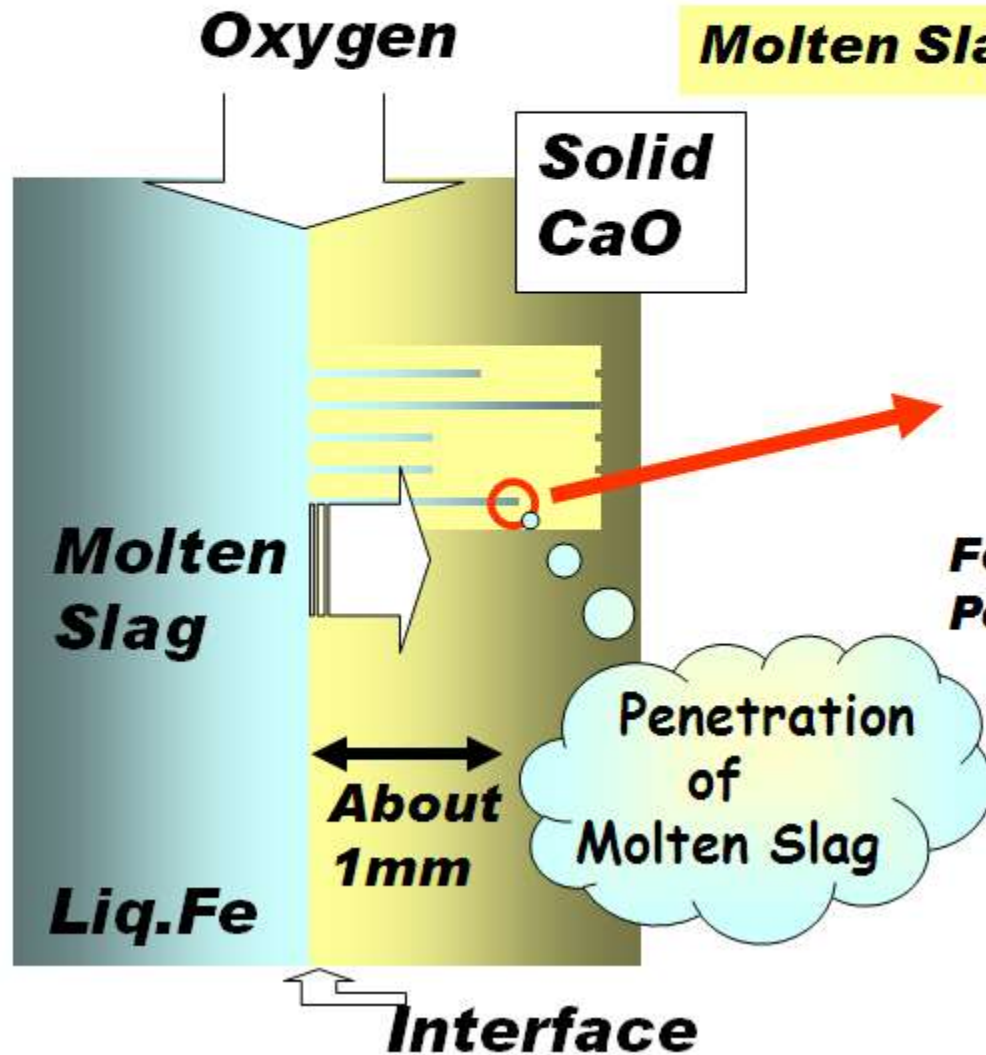
→  $\text{FeO} + \text{P}_2\text{O}_5$

→ Molten Slag

→ Penetration into  
Inner wall of CaO



# **“Capillary Refining” for Dephosphorization**

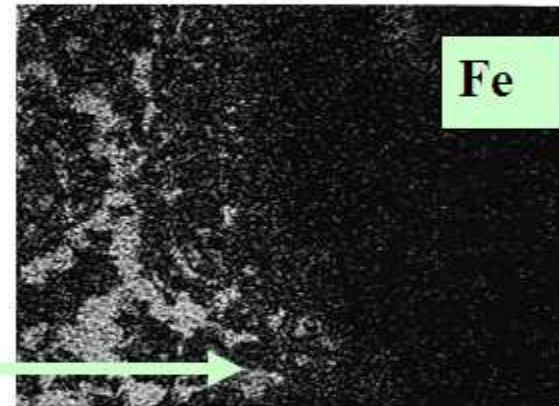


Penetration region of Molten Slag

**Molten Slag**

SEM

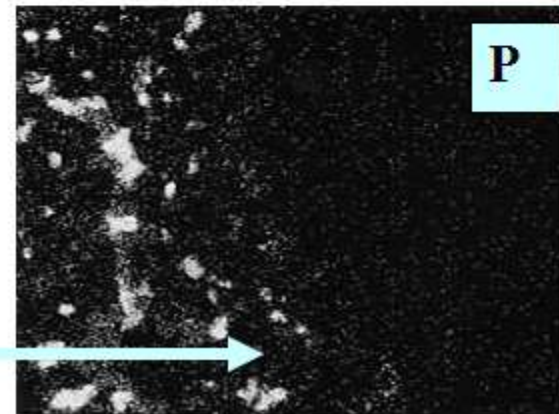
**Solid CaO**



**FeO Base Slag**

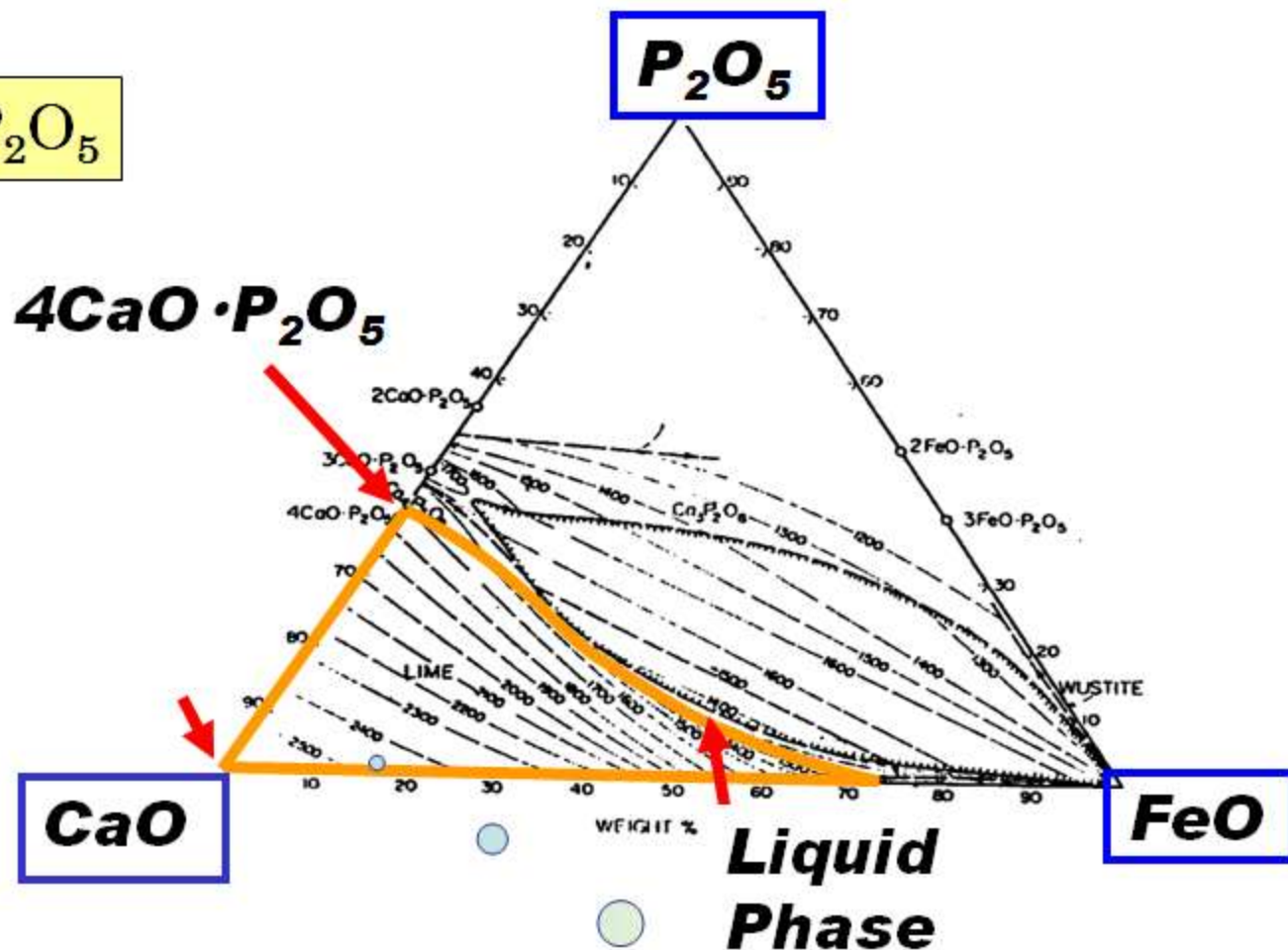
**Forefront of Penetration**

20μm



**P<sub>2</sub>O<sub>5</sub>**





Coexisting  
with Pure solid CaO

Keep activity of CaO  
to be unity.



**Solid & Liquid  
Coexist Phases**

**with De-P chemical reaction**

## Rotary Kiln

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

Porous  
 $\text{CaO}$

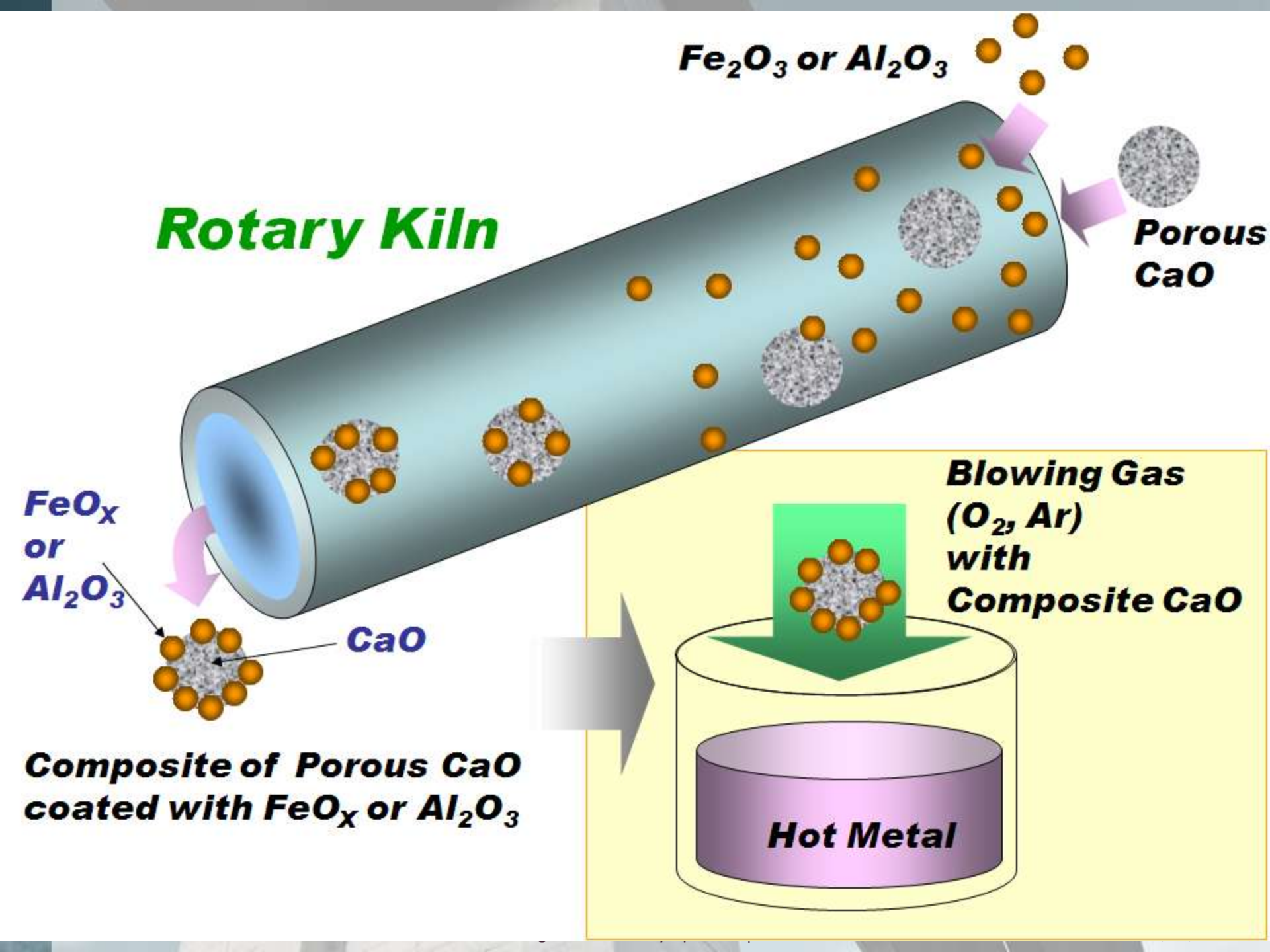
$\text{FeO}_x$   
or  
 $\text{Al}_2\text{O}_3$

$\text{CaO}$

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

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

Hot Metal

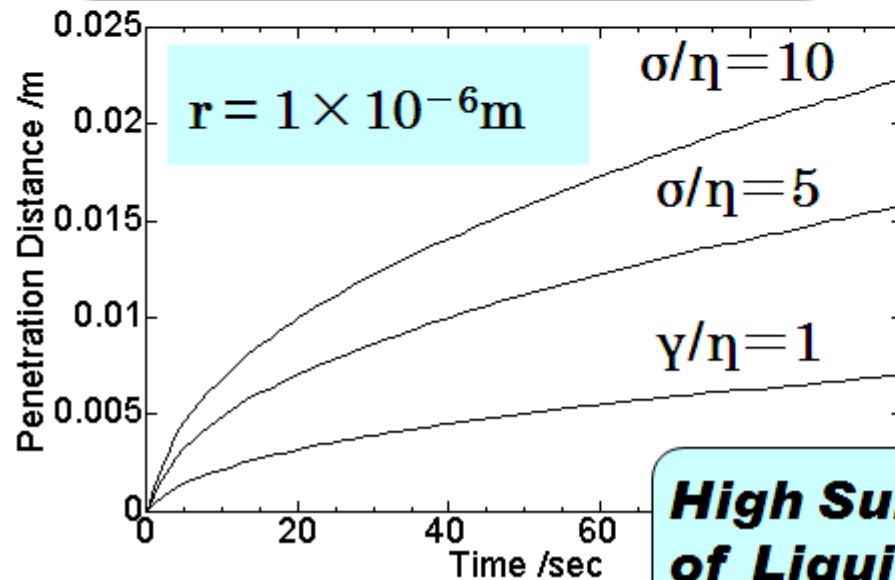
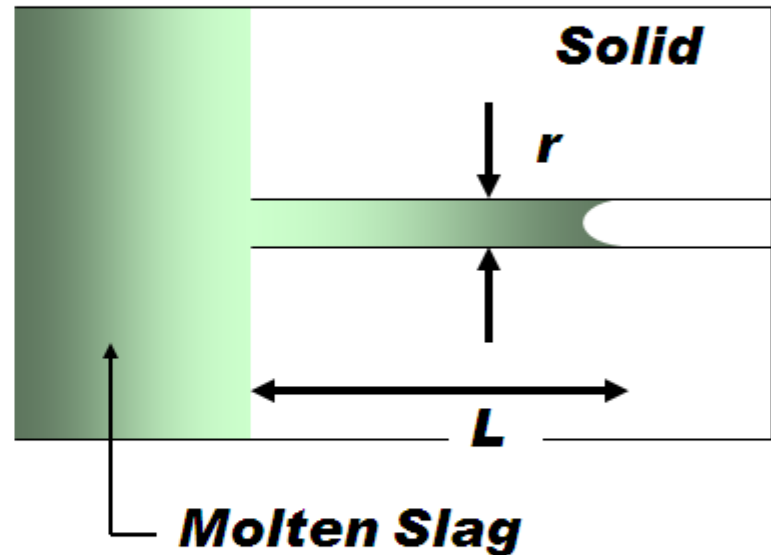




## Calculation of Penetration Flow Rate

$$L = \left\{ r \cdot \left( \frac{\sigma}{\eta} \right) \cdot t \right\}^{1/2}$$

***L***: Penetration Distance at time *t*  
***r***: Radius of Capillary  
 **$\sigma$  &  $\eta$** : Surface Tension & Viscosity of Molten Slag

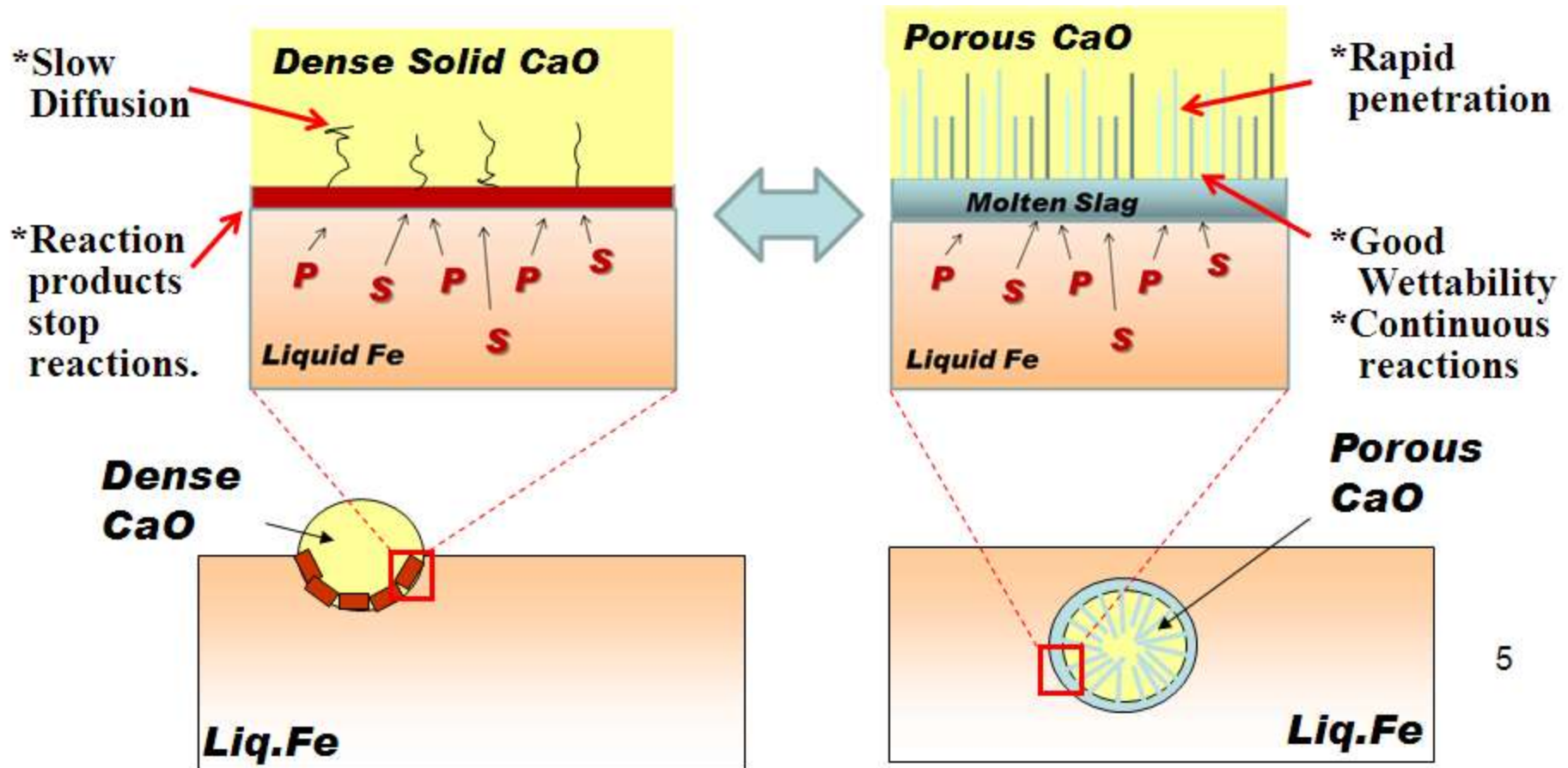


**Diffusion in solid is slow.**



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

# “Capillary Refining”



5