The importance of materials properties in high-temperature processes

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Physical properties &high-temperature processes

- **Phys. Chem. Properties- useful in solving problems with process control and product quality.**
- **First law of high temperatures**
- ***"At high temperatures everything reacts with everything else"***
- **Second Law:**
- ***"They react bloody quickly and situation worsens rapidly as the temperature increases".***
- **Many problems in high temp. processes- disaster never far away**

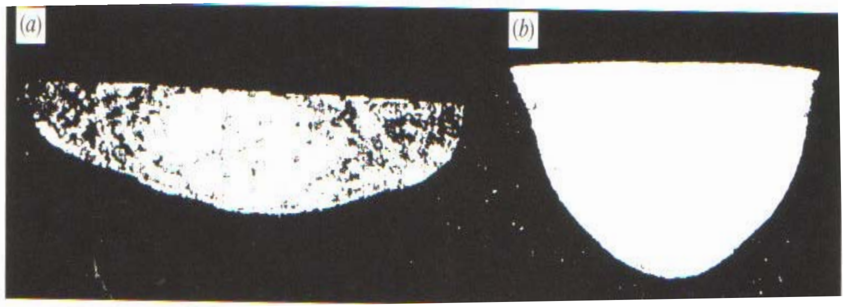
Example- variable weld penetration

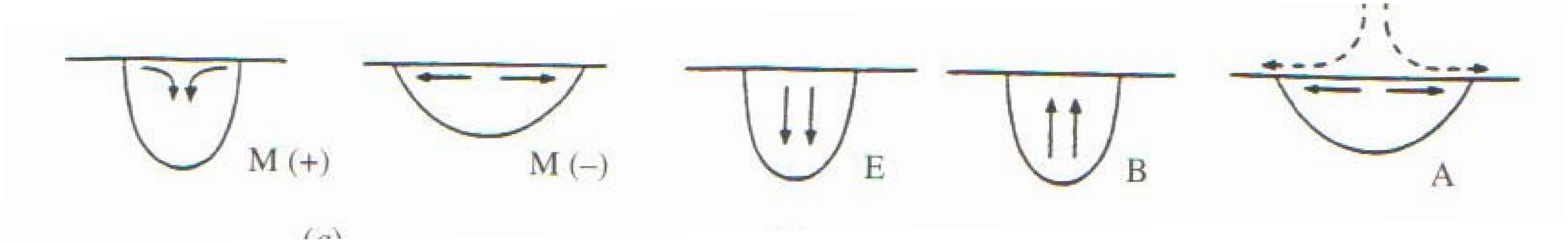
TIG/GTA welding-robotic process-many welds

-set up optimum welding-

Deep weld penetration

- **Change steel- meets spec. -→shallow welds**
- **Forces acting in pool**



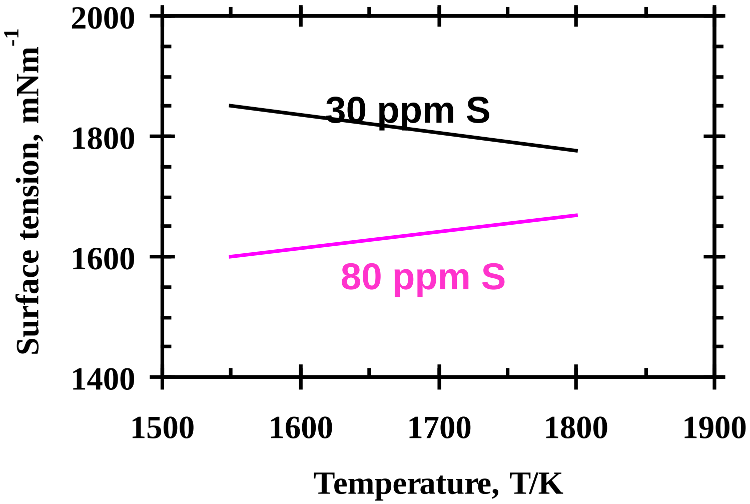


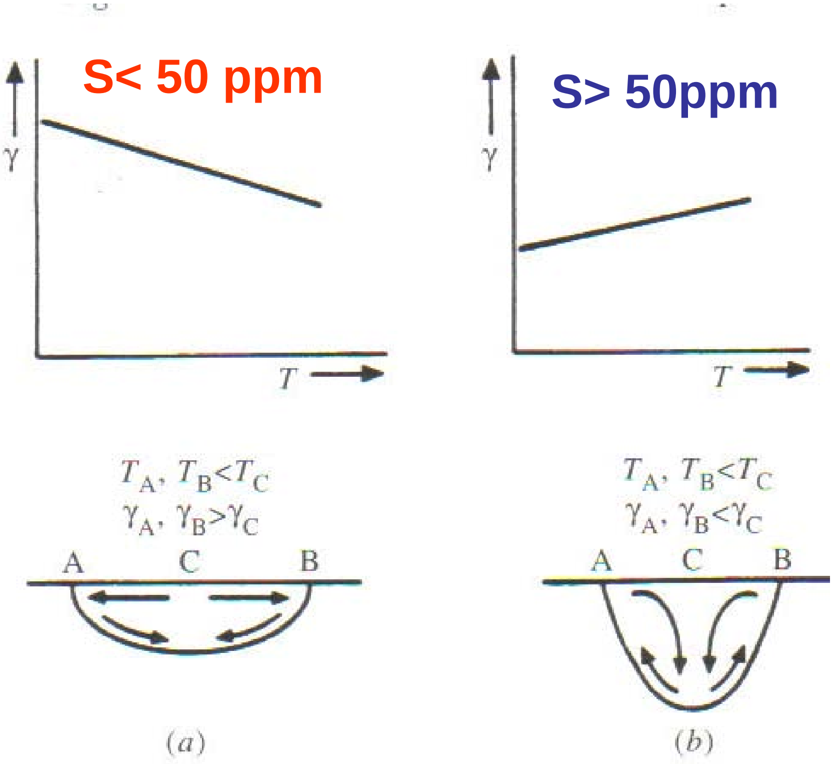
Effect of tiny differences in S

Surface tension >50steels

50ppm S →25% ↓ in γ

d γ/ dT → –ve to + ve





S< 50 ppm

S> 50ppm

- **Hot liquid → melt back**

<50 ppm S –flow outward-melt back-shallow weld

>50 ppm S –flow inward & down → deep weld

Slag properties and structure

Problem caused by ppm differences in S

Math models improved → insights to mechanisms

-Slags- are ionic

$4\underline{Al}_{steel}+3SiO_{2\ slag}=3\underline{Si}_{\ steel}+2Al_2O_{3\ slag}$

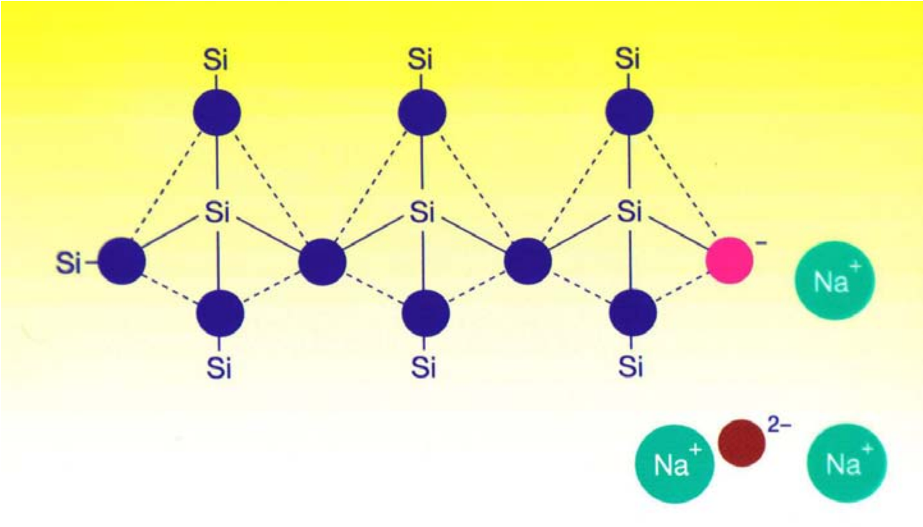
$$4\underline{Al} + 3Si^{4+} = 3\underline{Si} + 4Al^{3+}.$$

Slag props –depend on slag structure

Silicates- building block

Si- 4O tetrahedron with O joining 2 terahedra

Cations,Na^+ - break bonds



BOs, NBOs and free O’s

Alumino-silicates

Add Al_2O_3-network breakers↓

→ polymerisation ↑. $^{(4)}Al$

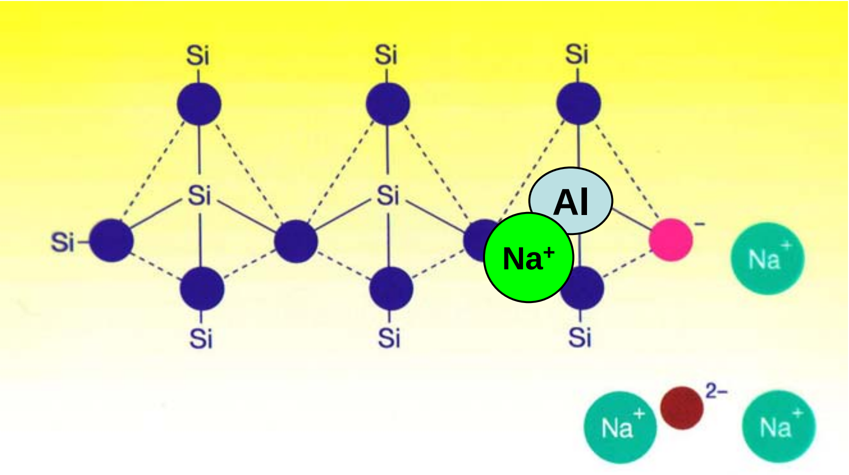
High Al_2O_3→some $^{(5)}Al$, $^{(6)}Al$

$NBO/T = 2\ (\Sigma X_{MO} + \Sigma X_{M2O} - X_{Al2O3})/(X_{SiO2} + 2\ X_{Al2O3})$

Q=(4- NBO/T) =measure of polymerisation

TiO_2 behaves like SiO_2?

Fe_2O_3,Cr_2O_3-behave as Al_2O_3 ?



Charge-balancing

Si^{4+}; Al^{3+}; →$(NaAl)^{4+}$;

Na^+ cannot act as network-breaker- polymerisation ↑

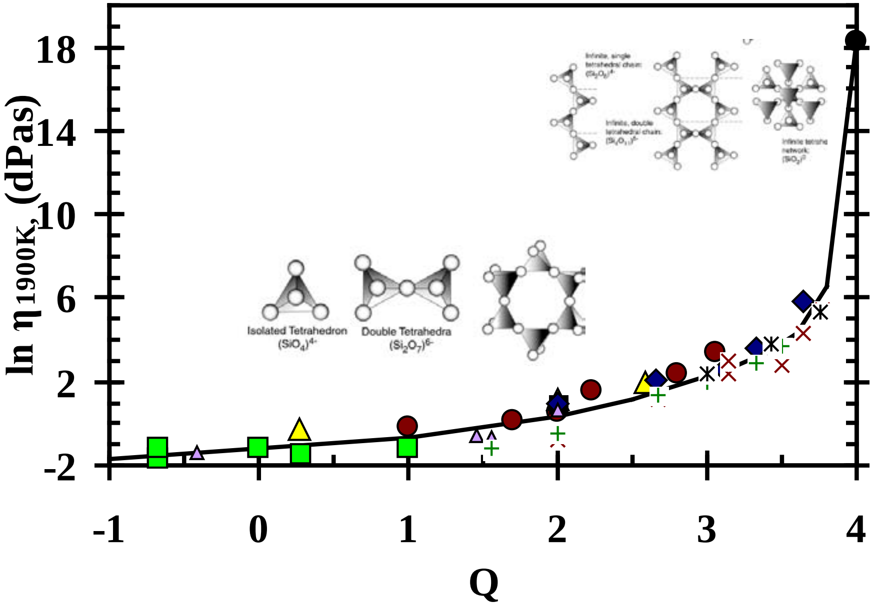
Effect of structure on slag properties

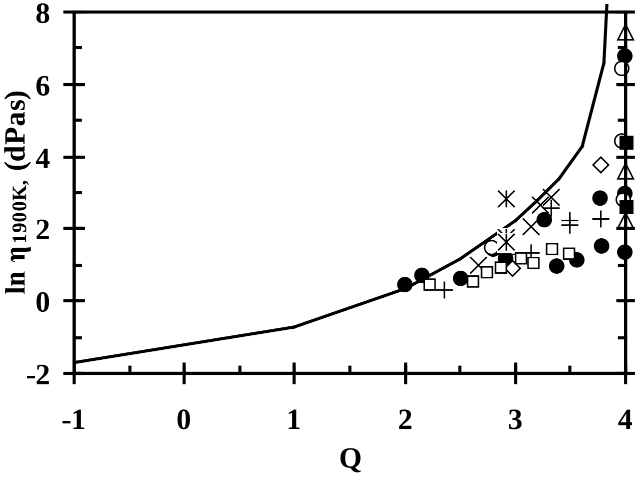
Polymerisation (Q) has great effect on props

Q↑ as %SiO_2 ↑ as CaO%↓

Alumino –silicates

May be Al-O bond weaker than Si-O bond





Factors affecting properties

Slags- crystals or glasses

Crystals-atoms fixed pos'n

Glasses-disorder- forms scl- high S_{config};

Nature cations→structure

Bond strength- (z/r^2)

$(z/r^2)\uparrow \rightarrow (Q^n \rightarrow Q^{n-1}+Q^{n+1})\uparrow$

$\rightarrow$ Coord no $({}^{(6)}N)\uparrow$

Size: elect cond. Diffusion

No. (n):Na_2O n=2;CaO,n=1

Effect of structure- props

1. **Viscosity(η) El cond (κ)/ Res(R)Diff coeff(D)**

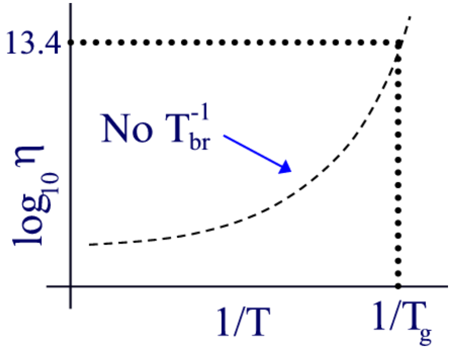
Liq: $\eta = A_A \exp(B_A/T)$

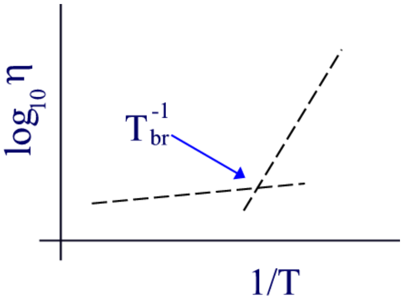
Scl: $\eta = A_V \exp(B_V/(T-T^o))$

1.Resistance cation movement

2. Mobility of cations size

Equivalent: η; R; (1/D)





ln η_{1900}; ln R_{1900};B_{η};B_{R} as f (Q)

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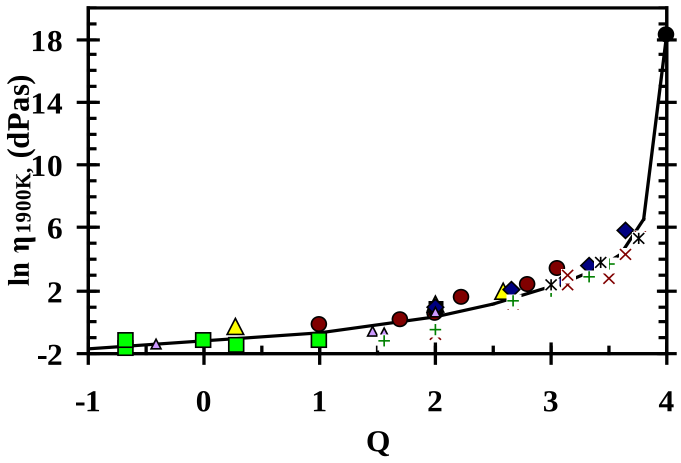
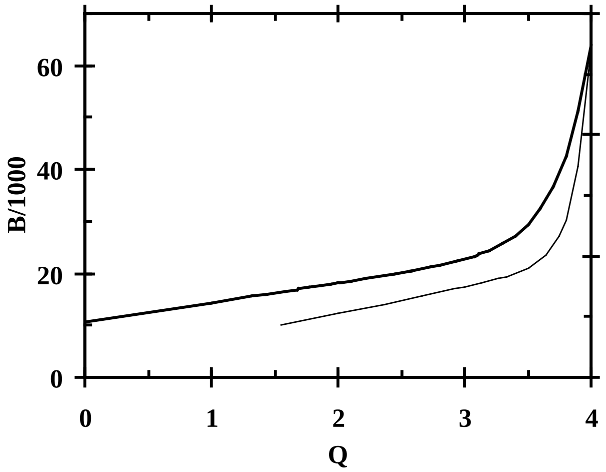
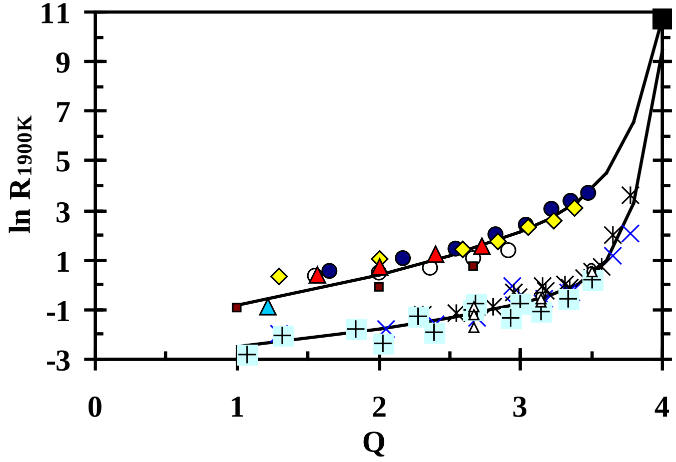
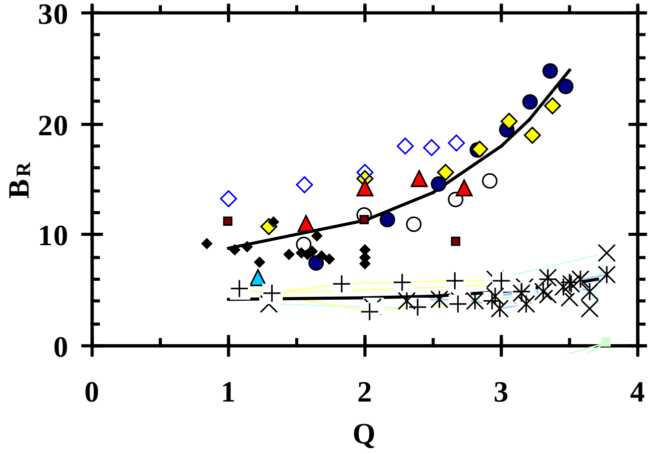






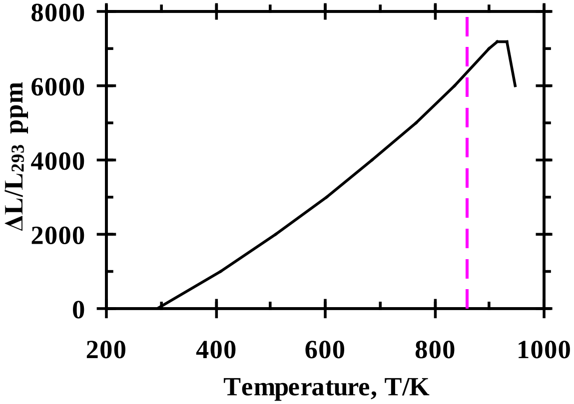


Density (ρ),Thermal expansion coeff (α,β) Surface and Interfacial tension (γ_{sl}, γ_{msl})

- α ↑ as Q↓ and (z/r^2) ↓
- α_{glass} ↑sharply at T_{g}-
- glass→ scl:
- T_g –T_{liq}: $\alpha_{scl} \approx 3\ \alpha_{crys}$:

ρ slightly affected by structure

$\rho_{crys} > \rho_{glass}$- better packing



γ_{sl}, γ_{msl} **surface** not **bulk property**

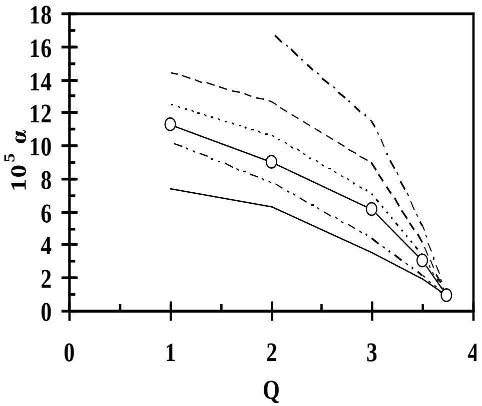
Surfactants- in surface layer *eg.* S,O in steel

slags, B_2O_3, CaF_2,K_2O, Na_2O

$\gamma_{msl} = \gamma_m + \gamma_{sl} - 2\varphi(\gamma_m\ \gamma_{sl})_{0.5}$

$\gamma_m \approx 4\ \gamma_{sl}$: γ_m most important

- S, O contents in metal



Thermal conductivity (k) thermal diffusivity (a)

Heat transfer over slag film

-complex-cond’n,rad’n, conv

Solid: $k_{eff}= k_{lat}+ k_R$.

$k_R=16\sigma n^2T^3/ 3\alpha^*$

liq glass: $k_R=10k_{lat}$.

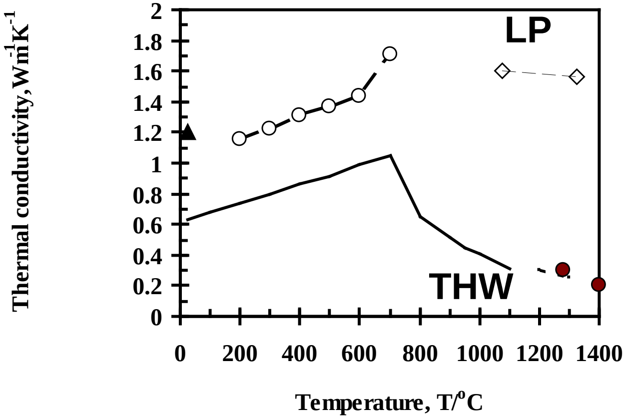
k_R↓ by (i) FeO add’n (ii) cryst

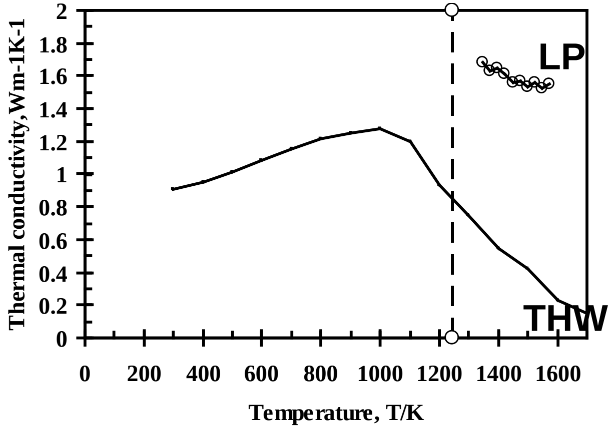
$k_{crys}\approx 2k_{glass}$

2 methods: LP and THW

$k_{LP} \approx$ 5-10 k_{THW}.

Problem un-resolved





Manipulation of properties for process optimisation-liquidus temp (T_{liq})

1. Liquidus temp (T_{liq})

Freeze linings- slag attack of refractory – Lurgi

-Slag coating of refractory

Slag splashing- BOS-LD

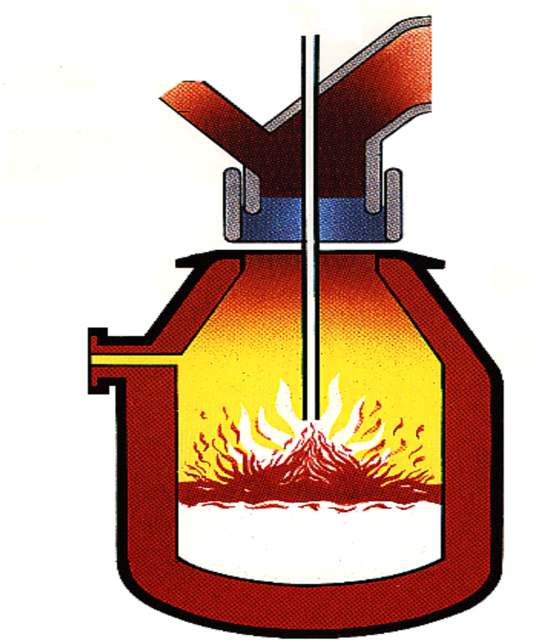
Pig $Fe+O_2 \rightarrow FeO$; $\underline{Si} \rightarrow SiO_2$

CaO added → slag

Great turbulence →

Extend refr life and minimise “downtime”

Optim. slag:13%FeO:8%MgO



Forms $MgO.Fe_2O_3$- high mp- >50,000 heats without re-lining

Manipulation of slag T_{liq}, viscosity(η)

Drainage rate- (1/ η)

Coal gasification

ash →↑ η slag

CaO added →↓ η

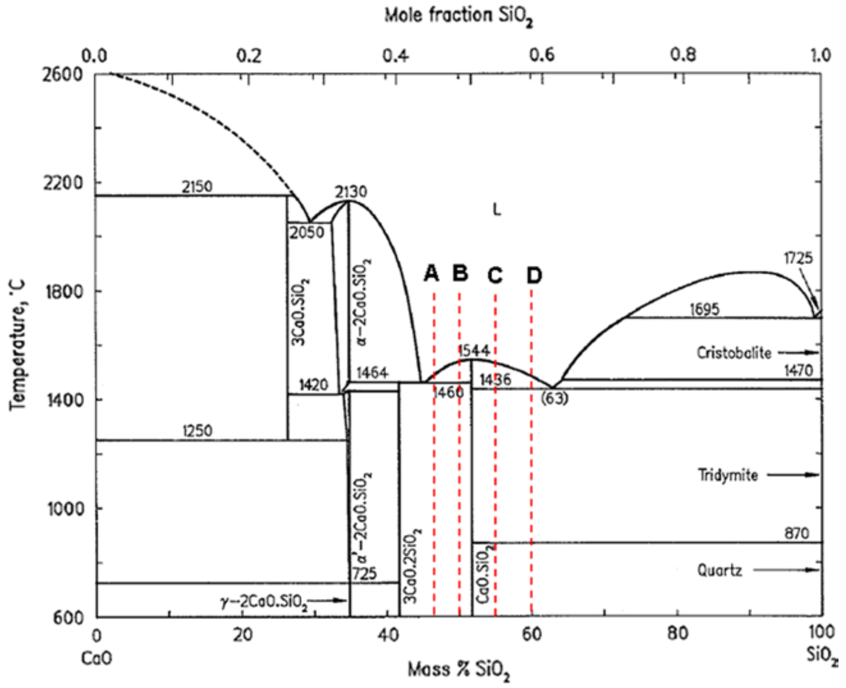
Low melting regions

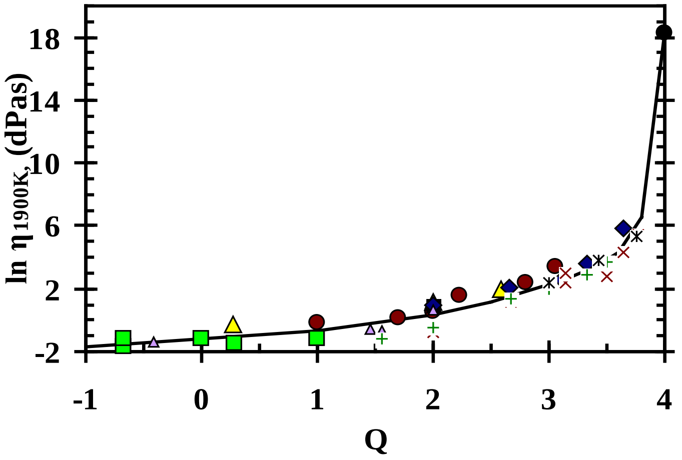
CaO- SiO_2 : X_{CaO} = 0.4-0.6

CaO- Al_2O_3 :X_{CaO}=(0.5-0.7)

Fixed amount CaO- disasters

Ladle glazes→inclusions





Manipulation of surface (γ_{sl}) and interfacial tension (γ_{msl})

Slag & metal entrainment

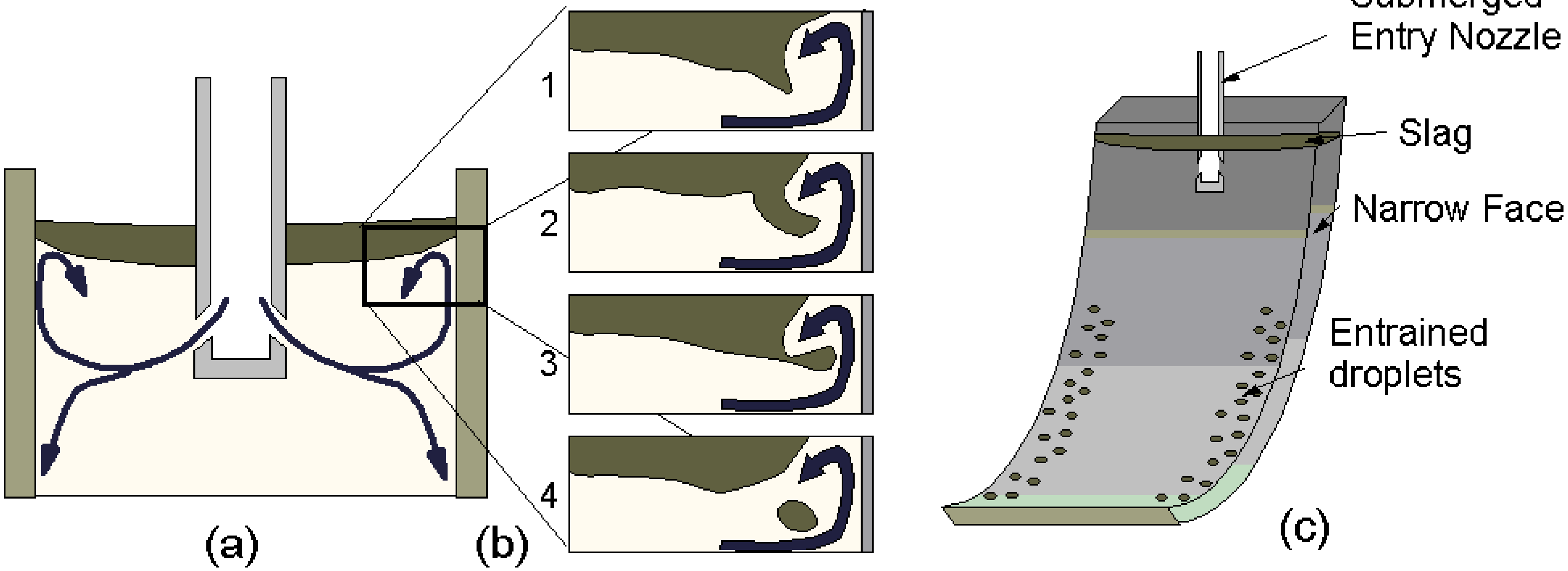
-**Loss of precious metals**

-**Inclusions in CC steel**

Velocity$_{metal}$ > Velocity$_{slag}$.

$$m_{entrap}=1.06\times10^{-7}\,(\eta_{sl})^{-0.255}.\,(\gamma_{msl})^{-2.18}$$

Min by incr η_{sl} and γ_{msl}.



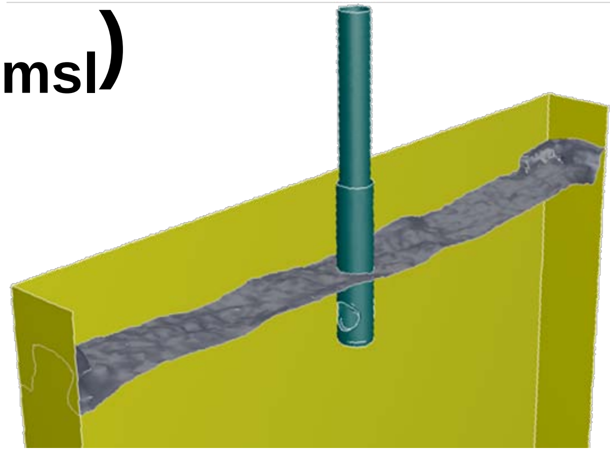
Manipulation of surface (γ_{sl}) and interfacial tension (γ_{msl})

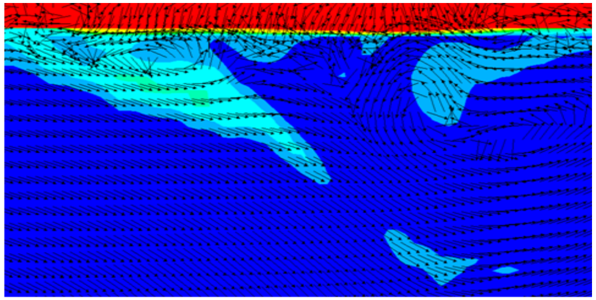
Math Model of CC process

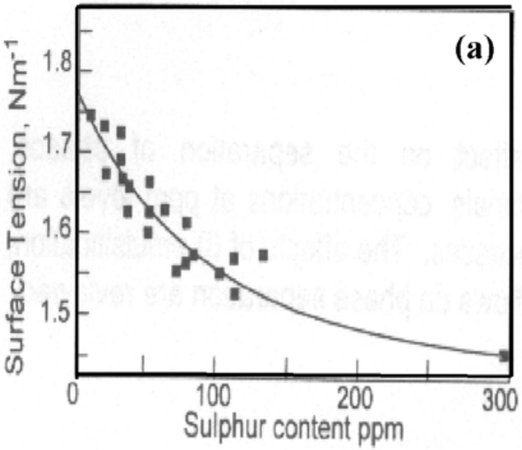
Predicts standing wave ,vortices, “*necking and detachment*”

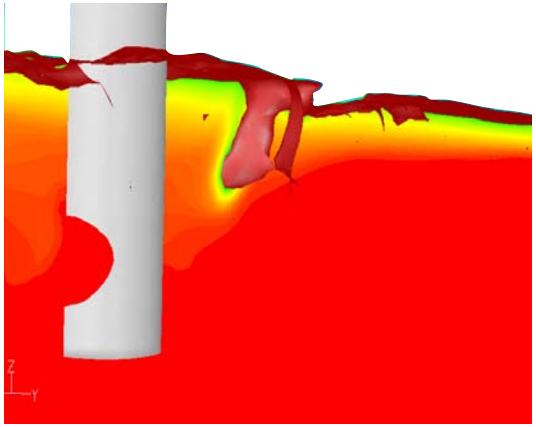
$\gamma_{msl} = \gamma_m + \gamma_{sl} - 2\varphi(\gamma_m \gamma_{sl})^{0.5}$

γ_{msl} ↑ *as S, O in metal* ↓
B_2O_3, K_2O, Na_2O ↓









Other problems involving surface and interfacial tension

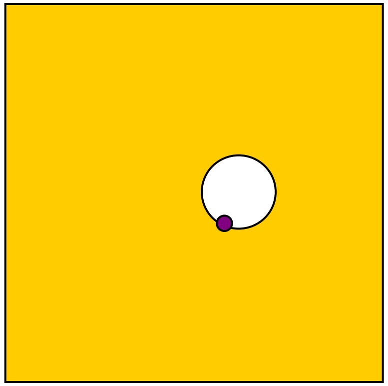
1.Removal of inclusions

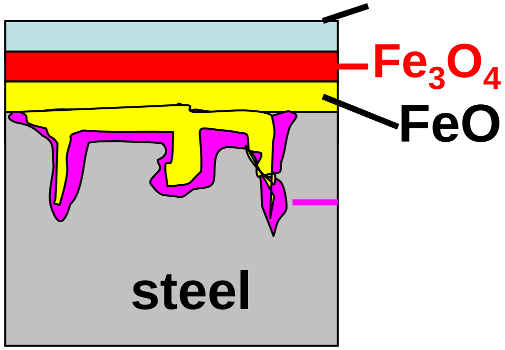
By Ar bubbling

2. Scale formation

Na_2O, K_2O cause slag to stick to metal-reacts with FeO→$FeSiO_3$ (scale)

3. Separation of metal droplets





Manipulation of heat transfer via freeze lining

Heat transfer-very complex

Cracking and stickers

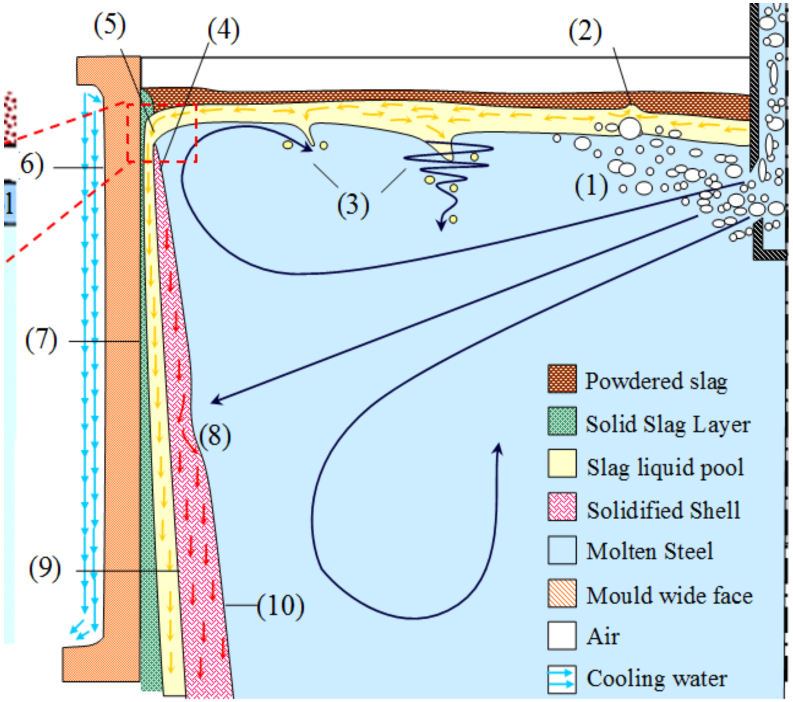
Heat flux, q – d_s, k_R,

$k_{cryst} \approx 2k_{glass}$; $q_{cryst} < q_{glass}$.

Cryst ↑→ k_R ↓

Heat flux manipulated by

1. $d_s \rightarrow T_{sol}$; $d_s \uparrow$ as $T_{sol} \uparrow$
2. % crystals in slag film



Harvesting enthalpy in slag

Steelmaking

Energy *ca.* 30% total costs

BOS slag –granulated – water spray on molten slag→ flame

H_2- decomposition of H_2O

Harvest H_2.

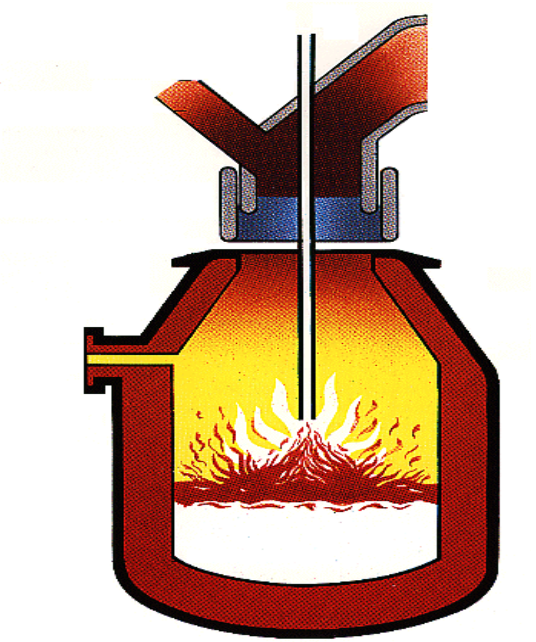
Problem – O_2 + H_2 mixture

Tata- reseach programme- estimated saving- 30 million $ p.a for average steelworks

Produced >70%H_2+N_2+CO_2

H_2 could be used for energy or as reductant

Pilot –ferrochrome plant



Discussion

- Vast range slag compositions high temp processes
- Compositions may change on daily basis
- Need for models to calculate props from chem comp.
- Models should include structural characteristics
- Can represent structure in terms of BO, NBO or Q or thermodynamic functions
- Challenge will be in representing certain structural features eg. Ti^{4+} prefers company of otherTi^{4+} to Si^{4+}

Conclusions

1. Slag properties proved very useful for solving process problems
2. Mathematical models can give insights into mechanisms and help solve problems.
3. Knowledge of factors affecting physical properties allows one to manipulate processes- including valorisation
4. Vast range of slag compositions in pyro-metallurgy - will need good models to estimate properties from chemical comp'n- where structure comes in.