

# Basic oxygen furnace based steelmaking processes and cleanliness control at Baosteel

L. Zhang<sup>\*1</sup>, J. Zhi<sup>2</sup>, F. Mei<sup>2</sup>, L. Zhu<sup>2</sup>, X. Jiang<sup>2</sup>, J. Shen<sup>2</sup>, J. Cui<sup>2</sup>, K. Cai<sup>3</sup> and B. G. Thomas<sup>4</sup>

Optical microscopy, total oxygen measurements and slime tests have been conducted to quantify the size distribution and amount of inclusions at various processing steps during basic oxygen furnace (BOF) based steel production at Baosteel. The effects on steel cleanliness of specific operational improvements during steel refining and continuous casting have been investigated. Such improvements to these processes and the resulting level of steel cleanliness at Baosteel are summarised in the present paper. Ladle slag reduction lowers FeO+MnO in the slag to below 5%, decreasing steel reoxidation by the slag. Calcium treatment by CaSi wire injection during ladle furnace (LF) refining is used to modify inclusions and improve submerged entry nozzle (SEN) clogging. Slag detection is employed at the ladle bottom during continuous casting. Flow control devices, CaO containing filters and high CaO based basic powder with  $\text{CaO/SiO}_2 > 4$  are used in the tundish to remove more inclusions. Several improvements to the castability and in the attainment of clean steel at mould operations have also been made. With this BOF based steelmaking process, impurity levels can be controlled to achieve total oxygen (TO) < 16 ppm, [S] < 5 ppm, [P] < 35 ppm, [N] < 29 ppm, [H] < 1 ppm in line pipe steels, and [C] < 16 ppm, TO < 19 ppm, [N] < 15 ppm in interstitial free (IF) steels.

**Keywords:** Clean steel, Inclusions, Impurity elements, Interstitial free steel, Line pipe steel

## Introduction

The importance of clean steel in terms of product quality is increasingly being recognised. Clean steel requires control of the size distribution, morphology and composition of non-metallic oxide inclusions in addition to the amount. Furthermore, sulphur, phosphorus, hydrogen, nitrogen and even carbon<sup>1,2</sup> should also be controlled to improve the steel properties. For example, formability, ductility and fatigue strength worsen with increasing sulphide and oxide inclusion contents. Lowering the carbon and nitrogen enhances strain aging and increases ductility and toughness. Hardenability and resistance to temper embrittlement can be enhanced by reducing phosphorus.<sup>1</sup> The definition of 'clean steel' varies with the steel grade and its end use. For example, interstitial free (IF) steel requires both carbon and nitrogen to be < 30 ppm; line pipe steel requires sulphur, phosphorus and total oxygen (TO) all to be < 30 ppm,

low hydrogen, low nitrogen and suitable Ca/S; hydrogen induced cracking (HIC) resistant steel requires  $\text{P} \leq 50$  ppm and  $\text{S} \leq 10$  ppm; and bearing steel requires the total oxygen to be less than 10 ppm.<sup>3</sup> In addition, many applications restrict the maximum size of inclusions,<sup>3,4</sup> so the size distribution of inclusions is also important. The control of steel cleanliness has been extensively reviewed by Kiessling in 1980 (Ref. 5), McPherson and McLean in 1992 (Ref. 6), Mu and Holappa in 1993 (Ref. 7), Cramb in 1999 (Ref. 4) and Zhang and Thomas in 2003 (Ref. 3).

Baoshan Iron & Steel Co., Ltd (Baosteel) is currently the largest steel company in China. Its annual steel production was 11.5 million tonnes in 2003, 11.9 million tonnes in 2004 and 14.0 million tonnes in 2005. With regard to the basic oxygen furnace (BOF) based steelmaking route, there are three 300 t and two 250 t BOFs; several steel refining units, including one CAS-OB unit (controlled argon stirring-oxygen blow), two RH (Ruhrstahl-Heraeus) degassers and one ladle furnace (LF); and two 1930 mm width slab casters, two 1450 mm width slab casters and one 2300 mm width heavy plate caster. Since 1990, efforts to improve steel cleanliness have focused on developing steelmaking practices to lower TO, N, S, P, H and C levels to achieve low carbon aluminium killed (LCAK) steel, ultra LCAK steel, such as IF steel, and line pipe steel, as well as further improve the castability by using cleaner steel or by using special methods such as slag detection

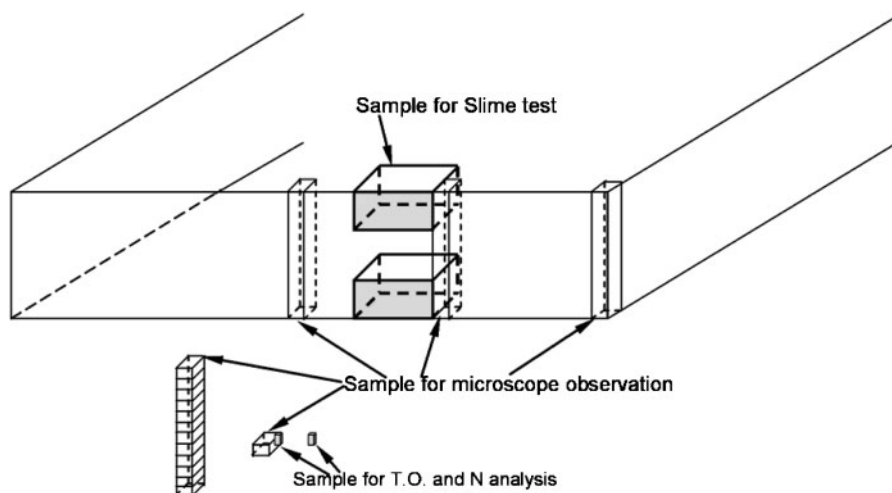
<sup>1</sup>Department of Materials Science and Engineering, Norwegian University of Science and Technology (NTNU), Alfred Getz vei 2, N-7491 Trondheim, Norway

<sup>2</sup>Baosteel Co., Shanghai 201900, China

<sup>3</sup>School of Metallurgical Engineering, University of Science and Technology Beijing, Beijing 100083, China

<sup>4</sup>Department of Mechanical and Industrial Engineering, University of Illinois at Urbana-Champaign, 1206 West Green St, Urbana, IL61801, USA

\*Corresponding author, email lifeng.zhang@material.ntnu.no



## 1 Sampling locations for continuously cast slab: TO total oxygen

during pouring, techniques to prevent nozzle clogging, more resistant refractory linings and breakout prediction systems at the caster. For LCAK steel and IF steel, the production process is BOF→RH→continuous casting (CC), and for line pipe steel, the process is BOF→RH→LF→CC. The present paper describes industrial clean steel production using the BOF based steelmaking process and steel cleanliness control at Baosteel.

## Experimental method and examination of inclusions in steel

### Experimental methods

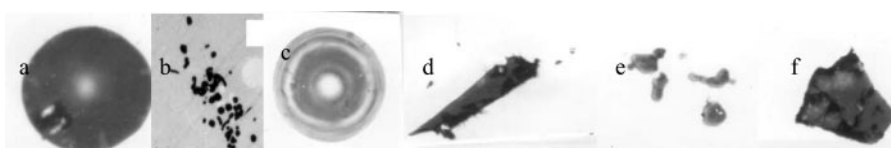
In the present work, several slag and molten steel samples were taken before, during and after steel refining, from the ladle, tundish and mould, and samples were removed from various locations in the slab. Ladle steel samples were taken 500–600 mm below the top slag in the ladle, tundish steel samples from 300 mm above its outlet and mould steel samples from 150 mm below the meniscus and 300 mm away from the submerged entry nozzle (SEN) outports. The sampler was a cylindrical steel cup with a cone shaped copper cover to protect it from slag entrainment during immersion. Attached to a long bar, the sampler was immersed deep into the molten steel, where the copper melted and the cup was filled. Small steel samples from the ladle, tundish and mould, 80 mm in length and 30 mm in diameter, were machined into 5 (dia.) × 5 mm cylinders for TO and nitrogen analysis, and 20 (dia.) × 15 mm cylinders for microscope examination. The steel powders resulting from machining were used for analysis of the carbon, phosphorus and sulphur contents. Large steel samples from the ladle and tundish, 200 mm in length and 80 mm in diameter, were machined into 60 (dia.) × 150 mm cylinders; the steel was dissolved to

extract the inclusions using the slime test,<sup>3</sup> which is a method of extracting inclusions from steel via electrolysis, leaving the basic components such as CaO, MnO, MgO, etc. In the case of slab samples, as shown in Fig. 1, 20 × 20 mm square section bars were taken through the whole thickness (250 mm), and were cut into 10 small pieces for microscope examination, TO and nitrogen measurement. Finally, 70 × 70 × 150 mm steel samples were cut from the slab for slime extraction, after the scale and the first few millimetres of the surface were machined off. Analysis included the chemical composition of slag and steel samples, microscope examination of microinclusions, slime extraction of macroinclusions and SEM analysis of the morphology and composition of inclusions. Inclusions on the section surface of ~300 steel samples from the ladle, tundish and slab were also investigated. On each sample, 300 random areas with a diameter of 0.3 mm were examined under the microscope to give the number and size of inclusions; thus, 21.2 mm<sup>2</sup> total area was observed for each sample.

In the present work, 'macroinclusions' were those greater than 50 μm in diameter. Most of these were detected in the residues extracted by electrolytic isolation ('slime test') from the larger steel samples. The 'microinclusions' data derive from microscopic assessments carried out on planar sections, most of which were smaller than ~50 μm.

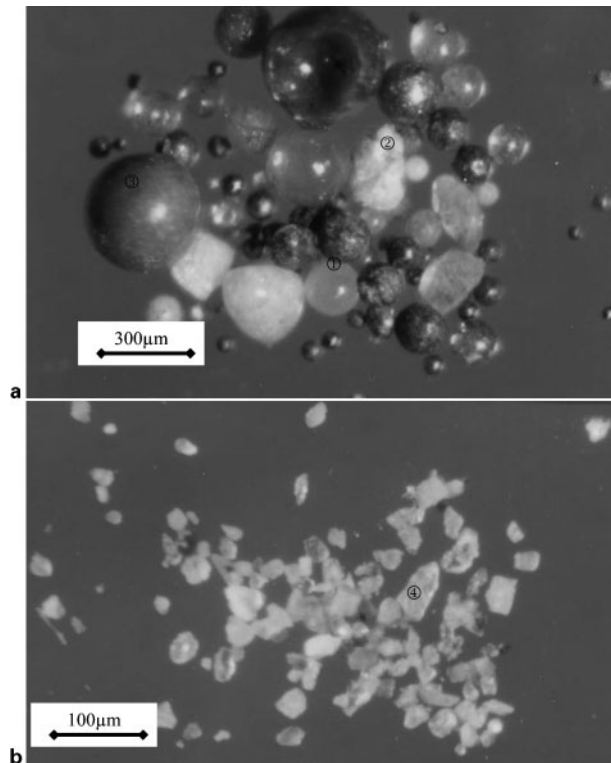
### Morphology and composition of typical inclusions

The morphology, composition and likely sources of typical inclusions found in LCAK steel samples from the ladle, tundish and mould are shown in Figs. 2 and 3 and given in Tables 1 and 2, respectively. The morphologies included: (a) angular aluminate (Fig. 2d and f and Fig. 3b); (b) alumina cluster (Fig. 2b and e); and (c)



a ladle; b tundish; c, d mould; e, f slab

## 2 Typical inclusions from given samples examined by microscope (see Table 1)



a tundish; b slab

### 3 Typical inclusions from given samples extracted using slime method (see Table 2)

spherical silicate (Fig. 2a and c and Fig. 3a). The possible sources were deoxidation products, reoxidation products, slag entrapment or broken refractory lining bricks. Inclusions larger than 50 μm in LCAK steel and line pipe steel were now less than 1 mg/10 kg steel, which corresponds to <0.1 ppm TO. These large inclusions could induce serious quality problems owing to their size, even though their fraction was very small.

In line pipe steel, besides these common inclusions, many nanoscale TiN inclusions were found along grain boundaries. These nano TiN inclusions changed from square to ellipsoid if combined with Ti<sub>2</sub>O<sub>3</sub>, as shown in Fig. 4.<sup>8</sup>

### Amount and size distribution of inclusions

Three kinds of inclusion size distributions are shown in Figs. 5–7. Figure 5 illustrates the inclusion number per

unit two-dimensional section area according to microscope examination. Figure 6 illustrates the weight of large inclusions per 10 kg of steel extracted by the slime method, which is similar to the inclusion mass fraction in the steel. Inclusions extracted by slime tests that were smaller than 62 μm were suspended in water and their size distributions measured with a Coulter counter, to obtain a three-dimensional inclusion size distribution. The curves were extrapolated to ~120 μm, as shown in Fig. 7, by comparing the measured amount of extracted inclusions larger than 50 μm. The inclusion mass fraction was 66.8 ppm in the tundish, 57.7 ppm in the 20 mm thickness nearest the slab surface and an average of 51.9 ppm in the slab. This suggests that the inclusion content in the interior of the slab (i.e. except the outer 20 mm thickness of the slab) was 50.6 ppm. The fraction of inclusions removed from the tundish to the slab was ~22%. Figure 7 also indicates that the number density (m<sup>-3</sup> of steel) of inclusions decreased with increasing size; nevertheless, in terms of volume (or mass) fraction, 10–40 μm inclusions constituted 68–79% of the total fraction of inclusions in the steel, and 40–60 μm inclusions constituted 9–19%.

The inclusion size distribution according to two-dimensional (2D) microscope examination (Fig. 5) can be converted into a three-dimensional (3D) distribution using

$$n_{3D} = \frac{n_{2D}}{d_p} \times 10^{12} \quad (1)$$

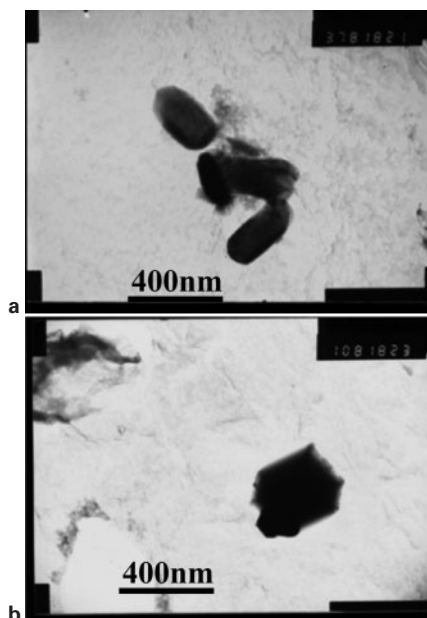
where  $n_{2D}$  is the number of inclusions mm<sup>-2</sup> of steel surface area,  $d_p$  is the inclusion diameter in μm and  $n_{3D}$  is the number of inclusions m<sup>-3</sup> of steel volume. This expression assumes that each inclusion is approximately cylindrical in shape, with height (into the plane) equal to its observed diameter. The 3D inclusion size distribution in the tundish and slab converted from 2D examination by microscope is shown in Fig. 8. By assuming 3000 kg m<sup>-3</sup> inclusion density, the total mass fraction of these inclusions can be estimated to be 68.8 ppm in the tundish and 66.5 ppm in slab. This estimated inclusion mass fraction in the tundish is very close to the measured value of 66.8 ppm. Although the estimated inclusion mass fraction in the slab is larger than the measured value of 51.9 ppm, equation (1) can be used reasonably to convert the 2D size distribution into a 3D distribution.

Table 1 Typical inclusions in steel examined by microscope, corresponding to Fig. 2, wt-%

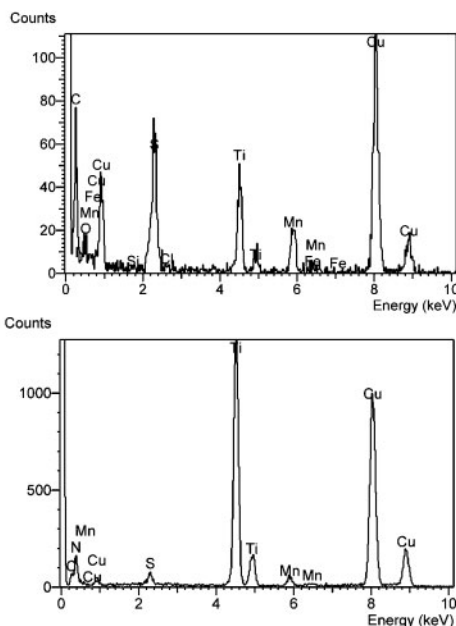
Inclusion in Fig. 2	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	CaO	MnO	FeO	MgO	K <sub>2</sub> O	Na <sub>2</sub> O	TiN	Possible source
a	1.2	56.4	0.5	5.8	20.3	10.1	0.3	5.1	0.3	Ladle slag
b	71.8	0.7	...	0.2	24.3	...	...	...	2.9	Deoxidation or reoxidation product
c	13.7	44.0	28.7	0.8	2.5	2.9	0.1	3.7	3.7	Mould flux
d	98.4	0.4	...	...	...	...	...	0.1	...	Deoxidation product
e	94.4	3.4	...	...	1.8	...	...	...	0.4	Deoxidation or reoxidation product
f	92.8	2.7	...	...	2.9	...	...	...	1.6	Refractory

Table 2 Typical inclusions in steel extracted using slime method, corresponding to Fig. 3, wt-%

Inclusion in Fig. 3	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	CaO	MnO	FeO	MgO	K <sub>2</sub> O	Na <sub>2</sub> O	TiN	Possible source
a, 1	2.7	83.2	...	9.1	3.7	1.1	...	...	0.2	Slag
	65.1	20.4	9.0	...	4.5	1.0	...	...	...	Slag
a, 3	24.0	29.0	4.1	19.7	16.4	1.4	0.7	1.3	...	Slag
b, 4	75.4	19.4	...	1.0	2.0	2.3	...	...	...	Deoxidation product



a compound inclusions with composition  $Ti_2O_3 + MnS$ ; b TiN inclusion



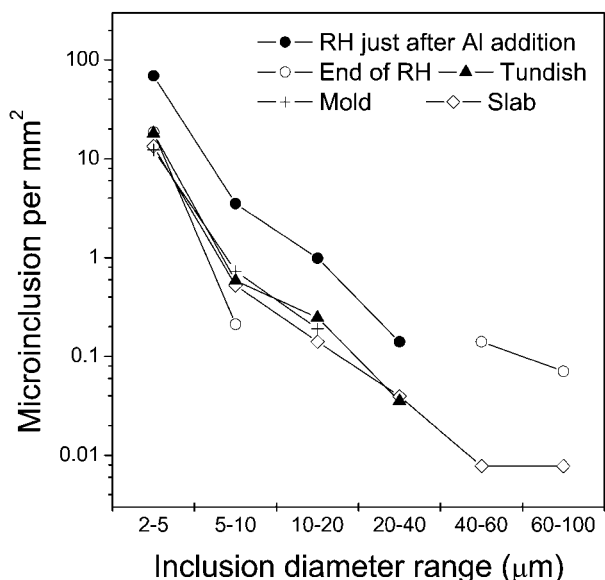
4 Nanoprecipitates in line pipe steel

Total oxygen measurement is an indirect method of evaluating oxide inclusions in a steel.<sup>3</sup> The total oxygen (TO) in the steel is the sum of the free oxygen (dissolved oxygen) and the oxygen combined as non-metallic inclusions. Free oxygen, or ‘active’ oxygen, can be measured relatively readily using oxygen sensors. It is controlled mainly by equilibrium thermodynamics with deoxidation elements, such as aluminium. If [%Al]=0.03–0.06, the free oxygen is 3–5 ppm at 1600°C. Because the free oxygen does not vary much, the total oxygen is a reasonable indirect measure of the total amount of oxide inclusions in the steel. Owing to the small population of large inclusions in a steel and the small sample size for TO measurement (normally <20 g), it is rare to find a large inclusion in a sample. Even if a sample contains a large inclusion, it is probably discounted because of the anomalous high reading.

Thus, the TO content actually represents the level of <50 μm small oxide inclusions only. The current TO in IF and line pipe steel slabs at Baosteel is <16 ppm. The TO in the ladle, tundish, mould and slab in two typical sequences of LCAK steel is shown in Fig. 9, indicating that the TO decreased from the ladle to the tundish, to the mould and to the continuously cast slab.

Inclusion distribution in slab

The distribution of inclusions through the thickness of the LCAK steel slab (250 mm thickness, 1300 mm width) measured by microscope examination is shown in Fig. 10. The data suggest that: (a) inclusions concentrated more in the 20 mm thickness nearest the slab surface; (b) inclusions sometimes accumulated at between one-half and one-quarter of the slab thickness from the inner radius; and (c) filters in the tundish were effective at lowering microinclusion levels. Further investigation by sulphur print detection indicated that this inclusion accumulation was more prevalent in the slab head and tail cast during unsteady conditions at the beginning and end of a sequence, as shown in Fig. 11. Microscope examination and SEM detection suggested that this inclusion accumulation was mainly induced by the entrapment of dislodged clogged materials from the SEN during ladle changes. The composition of a typical inclusion in the slab head containing both clogged material and some broken SEN surface refractory is given in Table 3. Examination also indicated that slag inclusions were mainly entrapped 0–50 mm from the surface of the slab.

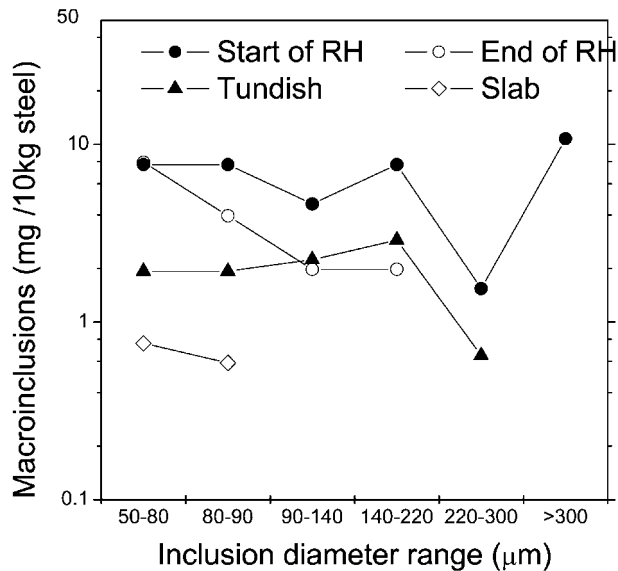


5 Microinclusion size distribution according to microscope examination: RH Ruhrstahl–Heraeus

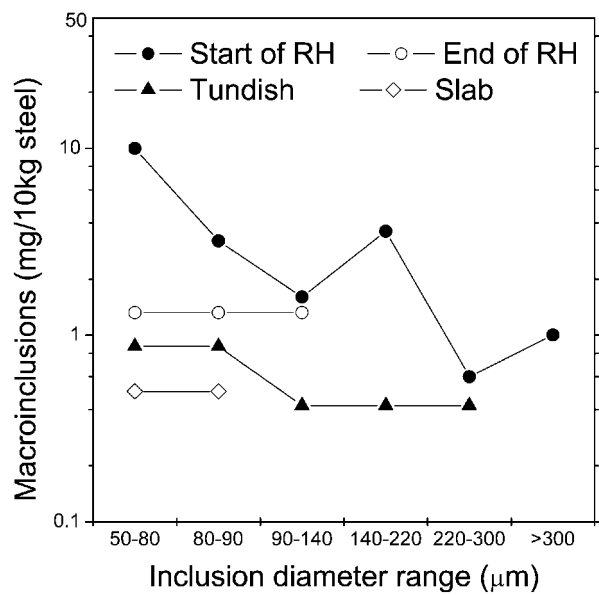
Ladle operations to remove more inclusions

Ladle slag reduction treatment

Reoxidation to form alumina in the ladle during steel refining is mainly caused by SiO<sub>2</sub> in the slag and lining refractory, and MnO and FeO in the ladle slag, by the following reactions



(a)



(b)

a one weir containing CaO filters and not touching bottom of tundish, two dams each side; b same as a except weir touching bottom

6 Size distributions of >50 µm inclusions according to slime extraction using given tundish flow control devices

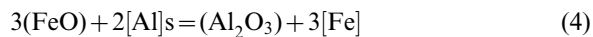
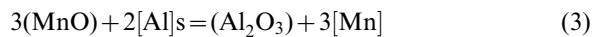
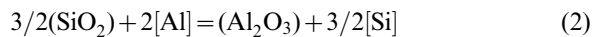
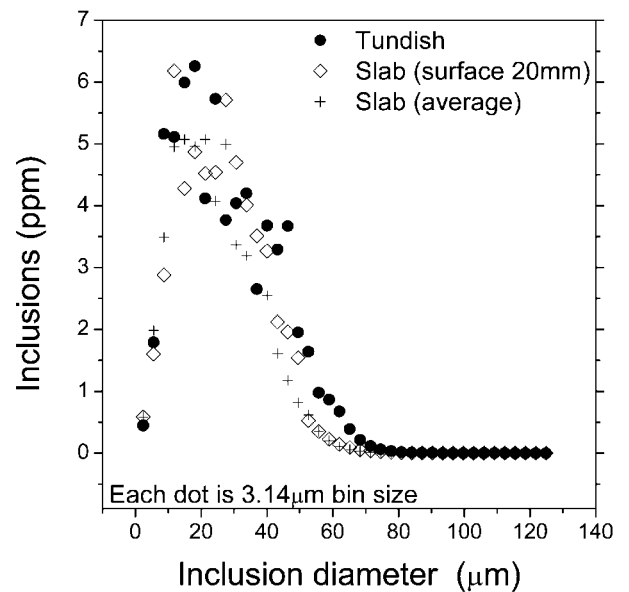
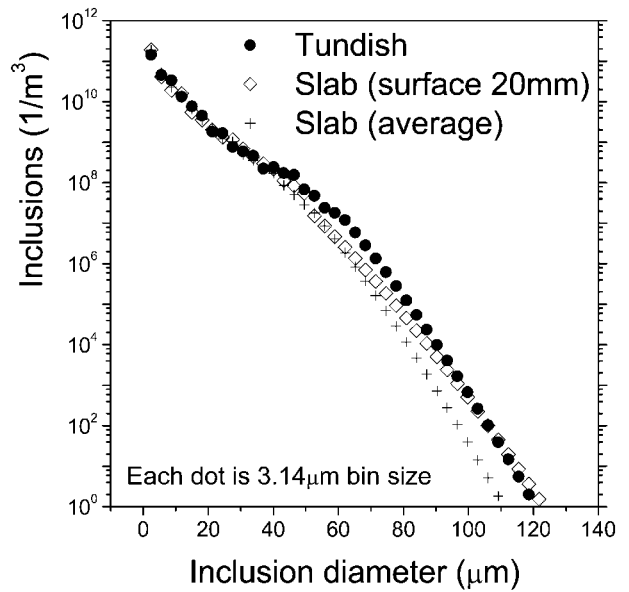


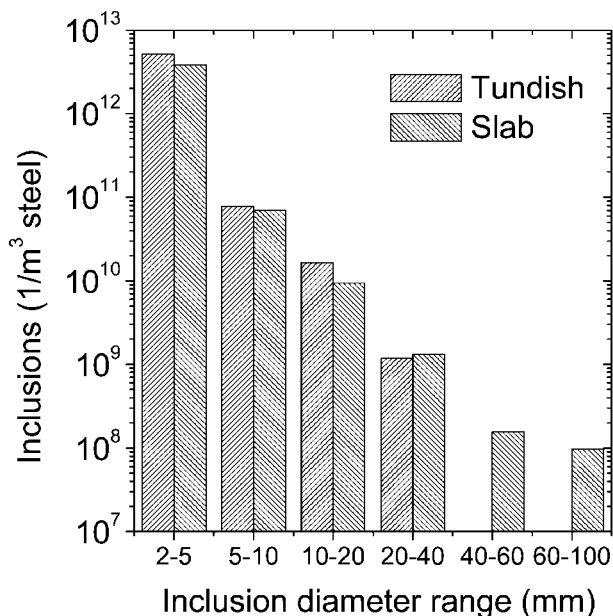
Table 3 Composition of submerged entry nozzle (SEN) clogging materials and typical inclusion accumulated at quarter thickness of slab head, wt-%

	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	FeO	Na <sub>2</sub> O	Cr <sub>2</sub> O <sub>3</sub>	CaO	ZrO <sub>2</sub>	S	F	C
Tundish powder	1.5	78.9	1.1	...	...	...	...	...	...	10.5
Mould flux	1.7	39.4	...	12.8	...	36.9	...	...	5.5	3.5
Initial layer of SEN	40.34	37.19	19.26	0.57	1.09	0.37	0.49	0.69	...	...
Clogging materials 1	97.47	2.37	...	0.08	...	...	...	...	...	...
Clogging materials 2	72.82	24.31	0.78	0.42	0.83	0.84	...	...	...	...
Clogging materials 3	92.26	3.65	3.54	0.16	...	0.62	...	0.03	...	...
Typical inclusion	90.93	2.24	3.92	...	...	0.38	1.78	0.74	...	...

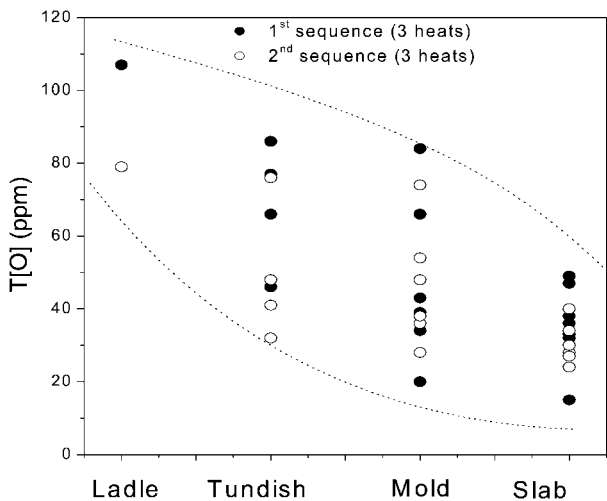


7 Inclusion size distribution evolution according to Coulter counter measurement of slime extracted inclusions

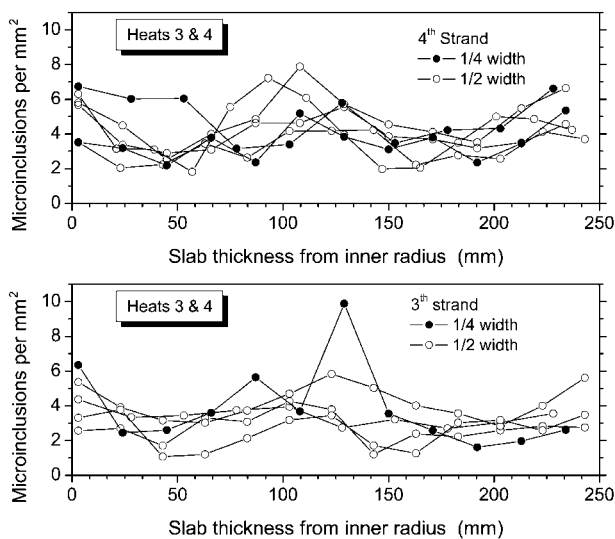
Slag reduction treatment is carried out by adding aluminium and lime onto the top of the ladle slag to reduce its FeO and MnO content. The effect of ladle slag reduction treatment on the TO content in the steel is shown in Fig. 12. A larger FeO+MnO content in the ladle slag corresponds to higher total oxygen. With the slag reduction treatment, MnO and FeO in the ladle slag were reduced to <5%, corresponding to <20 ppm TO in the tundish.



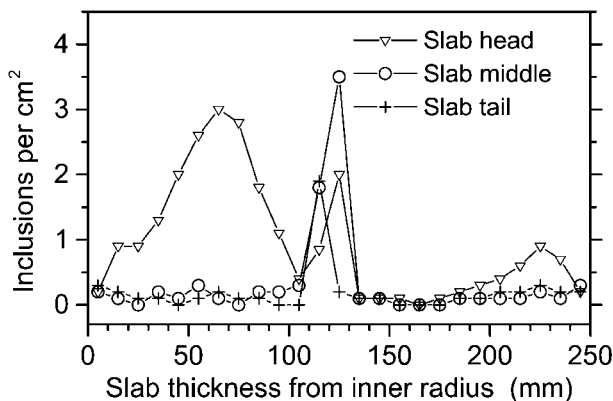
8 Three-dimensional size distribution of inclusions converted from two-dimensional microscope examination



9 Total oxygen in steel from ladle to slab



10 Microinclusion distribution along slab thickness with (strand 3) and without (strand 4) tundish filters: one weir and one dam each side in tundish



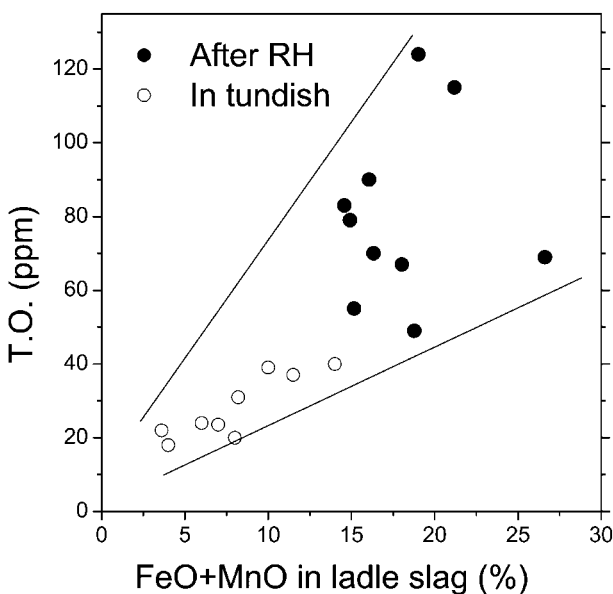
11 Inclusion distribution along slab thickness according to sulphur print

**RH treatment**

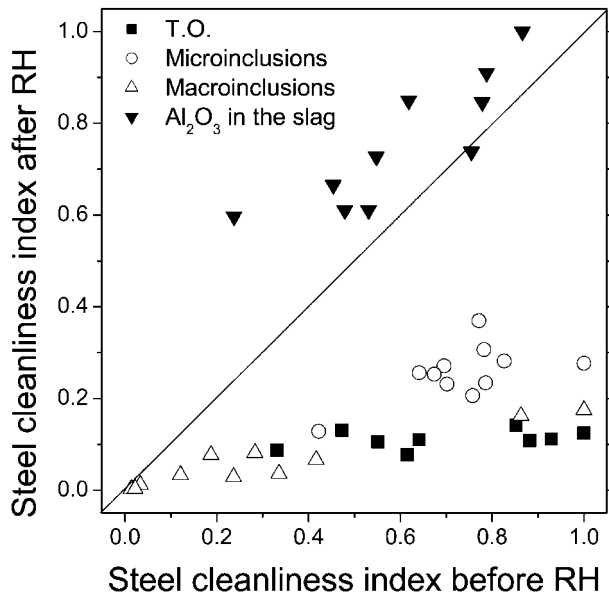
Figure 13 shows that RH treatment removed up to 90% of macroinclusions, 50–70% of microinclusions and 70–90% of the TO. Alumina in the ladle slag during RH treatment increased 8–13% from its original content. The results for different RH deoxidation times suggest an optimum treatment time of 8–12 min (Fig. 14). Beyond this optimum time, the oxygen removal efficiency may decrease owing to refractory lining erosion. Also, excessive stirring is detrimental because it may expose an ‘eye’ or slag free region of the steel surface to air reoxidation and perhaps even slag entrapment.

**Calcium treatment**

Nozzle clogging induces serious castability problems in aluminium killed steels, such as lowering the casting speed, inducing asymmetrical fluid flow and level fluctuations in the mould, thus entrapping more inclusions, and sometimes causing a breakout. Removing more inclusions before continuous casting is the best way to prevent nozzle clogging, and is the only approach for steels with very strict requirements on formability, because calcium treatment at the ladle may generate new hard inclusions.<sup>9</sup> For other aluminium killed steels, and

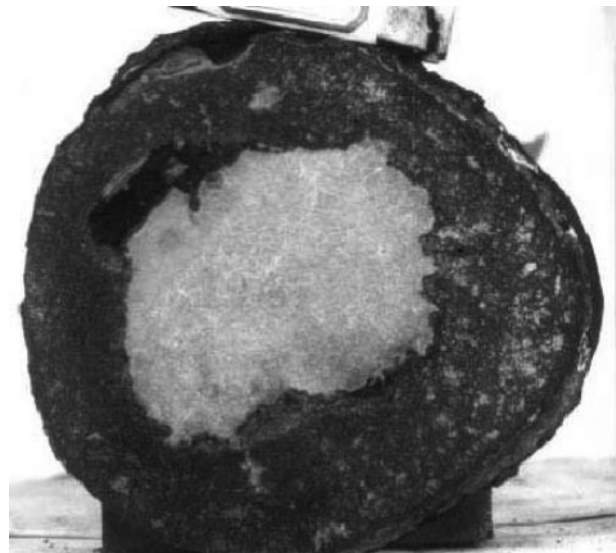


12 Effect of FeO and MnO content in ladle slag on TO in steel



13 Steel cleanliness before and after RH treatment: large index means poor cleanliness

for greatly desulphurised line pipe steels, calcium treatment can be used to improve SEN clogging. At Baosteel, CaSi wire is fed into the molten steel during ladle refining. Alumina reacts with CaO, forming calcium aluminates. If the generated calcium aluminates have a low melting point, then clogging is improved. The possible compound inclusions generated by calcium treatment include  $CA_6$ ,  $CA_2$ ,  $CA$ ,  $C_{12}A_7$  and  $C_3A$ , where C and A represent CaO and  $Al_2O_3$ , respectively. The first two should be avoided owing to their high melting point over  $1700^\circ C$ . Adding too much or too little calcium can also induce SEN clogging, however. An example of SEN clogging during continuous casting of a calcium treated heat with 16 ppm [Ca] after calcium treatment is shown in Fig. 15. The white centre is steel, and the black surround is clogging, with a composition

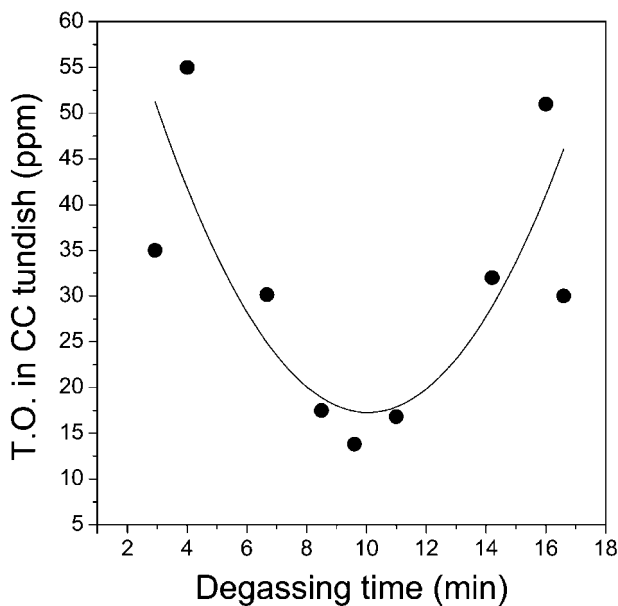


15 Submerged entry nozzle (SEN) clogging in heat with calcium treatment during ladle refining

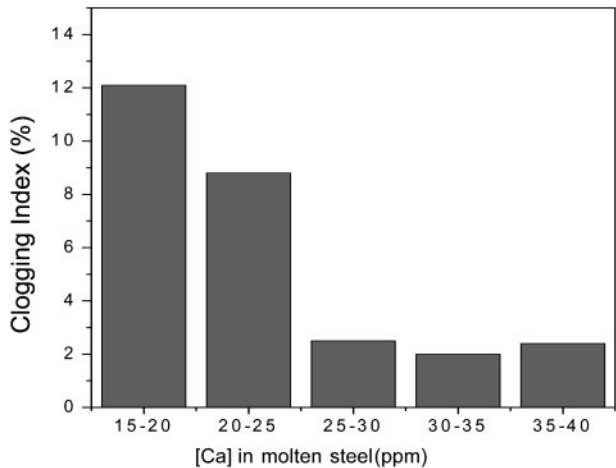
of mainly  $CA_2$ . Current practice at Baosteel indicates that [Ca] should be  $>25$  ppm in order to prevent solid alumina based inclusion clogs (Fig. 16). Too much calcium can also generate CaS with a high melting point ( $2450^\circ C$ ). Increasing dissolved aluminium also decreases the oxygen activity, generating sulphide inclusions. Too much sulphur in the steel and too low a temperature also enables CaS generation. Baosteel practice indicates that  $<50$  ppm [Ca] in the steel can prevent CaS generation, and  $[Ca]/[Al] > 0.09$  favours prevention of nozzle clogging (Fig. 17). Hence, [Ca] needs to be controlled within the range 25–50 ppm, and  $[Ca]/[Al] > 0.09$ , to avoid nozzle clogging problems.

**Ladle slag detection during pouring**

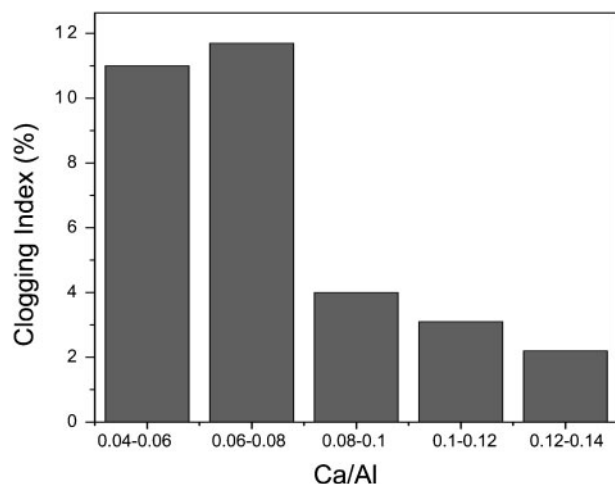
An electromagnetic slag detection system<sup>10</sup> is used at the bottom of the ladle during pouring to minimise slag carryover at the end of pouring, induced by the swirl flow. Slag inclusions in the steel are decreased and consequently the steel yield is improved, as shown in Fig. 18. The steel left in the ladle is 1 t less than before.



14 Effect of RH degassing time on TO in tundish



16 Effect of calcium content in steel on nozzle clogging



17 Effect of Ca/Al ratio on nozzle clogging

## Tundish metallurgy and caster operations to improve steel cleanliness

### Flow control devices

The two strand tundish investigated has a steady operating capacity of 60 t, 1.2 m depth and MgO based basic refractory lining. The effect of dams and filters on inclusion removal has been investigated. Table 4 indicates the removal of TO, microinclusions and macroinclusions between the ladle after RH treatment and the tundish. More inclusions were removed in the tundish with each side having two dams, and a weir containing filters, than in the tundish with only one dam, and a weir without filters. The filters were effective at removing more TO and macroinclusions. There was no clear difference in steel cleanliness whether the weir touched the bottom or not (Fig. 6).

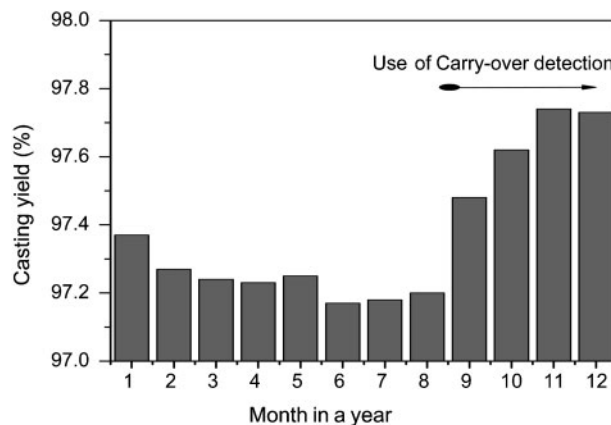
**Table 4 Measured inclusion content and removal fractions from ladle to tundish\***

	Heat 1	Heat 2	Heat 3
<b>Total oxygen (TO), ppm</b>			
Ladle	103	70	67
Tundish	81	63	44
Removal fraction	21%	10%	34%
<b>Microinclusions, mm<sup>-2</sup></b>			
Ladle	7.2	8.4	10.8
Tundish	5.1	6.0	3.2-5.1
Removal fraction	29%	28%	53-70%
<b>Macroinclusions, mg/10 kg steel</b>			
Ladle	138.9	66.0	94.3
Tundish	36.9	32.6	9.4
Removal fraction	74%	51%	90%

\*Heat 1: one weir (no filters) and one dam each side; heat 2: one weir (containing CaO filters) and one dam each side; heat 3: one weir (containing CaO filters) and two dams each side (weir did not touch tundish bottom).

**Table 5 Parameters of CaO based basic tundish flux**

CaO/SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub> , %	MgO, %	F, %	Melting point, °C	Viscosity at 1400°C, Pa s
4.0-8.0	30-50	5.0-10.0	<5.0	1200-1400	0.20-1.0
0.8-2.0	<10.0	<15.0	<5.0	1190-1350	0.20-1.0



18 Improvement of casting yield using slag carryover detection system at ladle

### Basic tundish flux

Plant experience found that MgO-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> based basic tundish flux tended to freeze owing to its high melting point (>1400°C). This made it difficult to absorb inclusions, and also could not effectively prevent air absorption. Instead, CaO-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> based fluxes were developed. The effect of the CaO/SiO<sub>2</sub> ratio on castability and steel cleanliness has been investigated. The main characteristics of the fluxes are given in Table 5. The molten steel temperature and TO in the tundish during IF steel casting are shown in Fig. 19. The steel temperature during a ladle exchange period was more steady and lower TO was achieved when the flux contained CaO/SiO<sub>2</sub>>4, compared with CaO/SiO<sub>2</sub><2. In addition, less erosion of the tundish and SEN refractory lining was found for the tundish flux with CaO/SiO<sub>2</sub>>4 than with CaO/SiO<sub>2</sub><2.

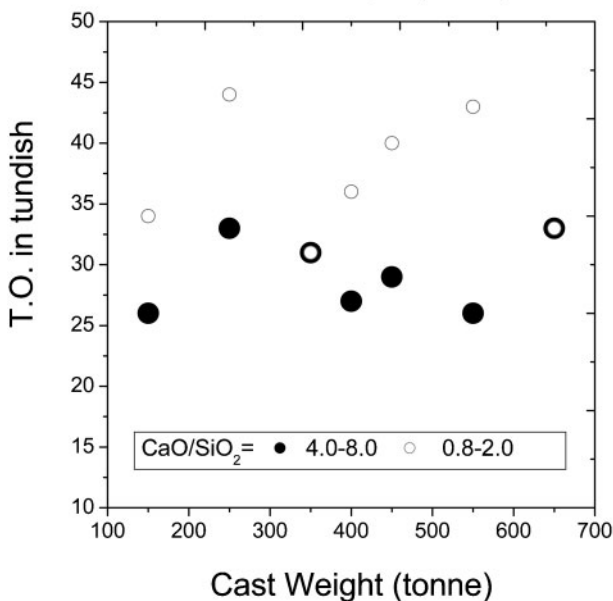
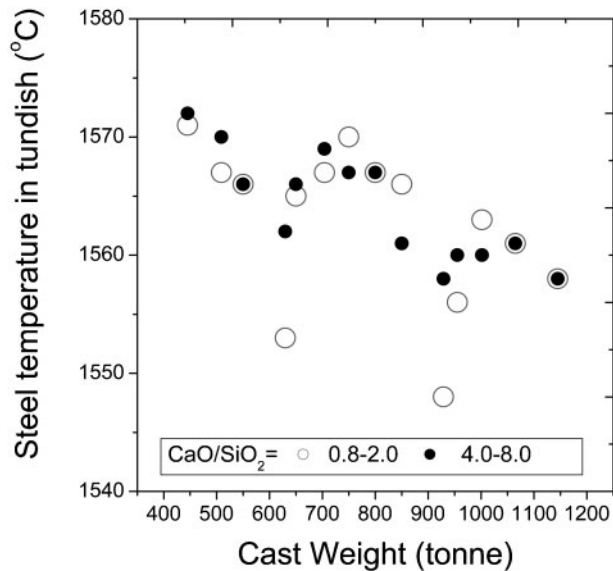
### Caster operations

Many techniques are used at the caster to produce ultraclean steel, including:

- low carbon, high viscosity mould flux for LCAK steel
- low sulphur and phosphorus content mould flux for line pipe steel
- mould level fluctuations controlled within  $\pm 3$  mm
- argon injection optimised effectively to protect molten steel from air absorption, and to maintain a stable double roll flow pattern in the mould
- SEN refractory lining chosen to prevent nozzle clogging and retard erosion by mould flux
- effective breakout prediction system implemented using three rows of thermocouples at the mould copper plates.

Since Baosteel developed its own breakout prediction system in 1999, all sticker breakouts have been predicted and avoided during the continuous casting of 3263





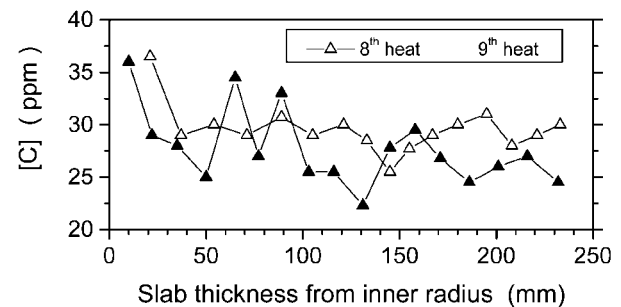
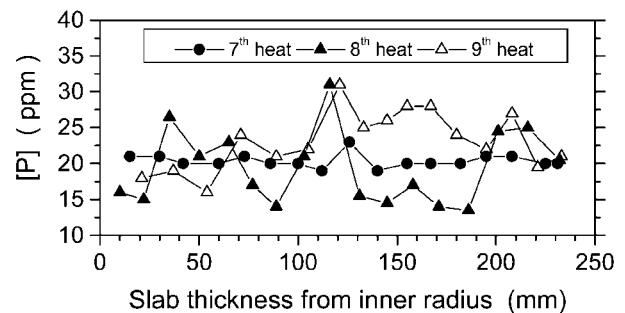
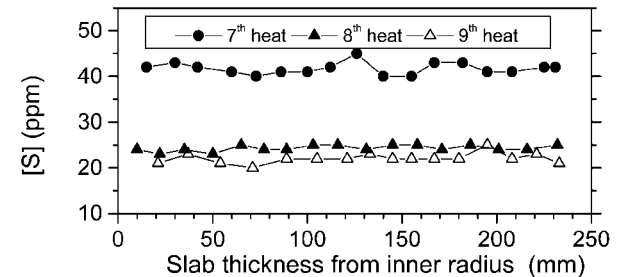
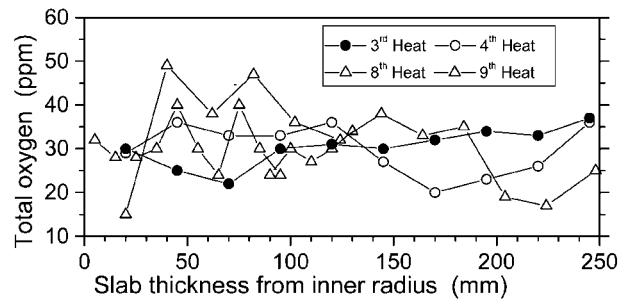
19 Temperature and total oxygen (ppm) of molten steel in tundish (four heats) during continuous casting using given tundish fluxes

heats. The false alarm rate is nine per 10 000 heats. This system has enabled a higher average casting speed, and fewer defects owing to cracks and slag entrainment during transient casting. Currently there are almost no sticker breakouts, only ~5 breakouts per year from longitudinal cracks.

## Control of nitrogen, carbon, sulphur and phosphorus in steel

### Nitrogen

Normally, a large nitrogen content at tapping tends to result in a large nitrogen content in the slab. Thus, the control of nitrogen should mainly focus on lowering the nitrogen content during BOF blowing and preventing nitrogen pickup during tapping, steel refining and continuous casting. Currently, at Baosteel, nitrogen during BOF steelmaking fluctuates from 11 to 43 ppm. Plant experiments indicate that when [N] is less than 30 ppm before RH treatment, [N] cannot be lowered further by RH treatment. The shrouding system is



20 Distributions of total oxygen, sulphur, phosphorus and carbon along slab thickness

critical to prevent air absorption, which is the source of nitrogen pickup. Oxygen pickup is always many times greater than the measured nitrogen pickup, owing to its faster absorption kinetics at the air/steel interface.<sup>11</sup> In addition, nitrogen pickup is faster when the oxygen and sulphur contents are low.<sup>12</sup> Thus, to reduce nitrogen pickup, deoxidation is best carried out after tapping, which is the current practice for clean steel grades at Baosteel. The current nitrogen content of IF steel and line pipe steel slabs is 15–30 ppm, and nitrogen pickup from ladle to tundish can be controlled below 1.5 ppm by optimised shrouding, argon gas injection and fibre sealing at the tundish and SEN.

### Carbon

The greatest decarburisation is for IF steel by RH treatment. Techniques to improve this operation include:

- optimising initial [C] and [O] before degassing into the ranges of 500–650 ppm and 300–450 ppm, respectively

- (ii) enlarging the snorkel diameter from 500 to 750 mm and increasing the argon flowrate from 1000 to 3000 NL min<sup>-1</sup>.

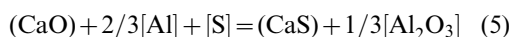
After RH treatment, [C] can be lowered to 10 ppm. The [C] pickup occurring during continuous casting is controlled below 6 ppm by the following techniques:

- (i) using low carbon, high viscosity mould flux, decreasing carbon pickup at the continuous casting mould from 5.5 to 1.8 ppm
- (ii) using carbon free ladle refractory lining
- (iii) using high basic, low carbon tundish flux (CaO/SiO<sub>2</sub>>4)
- (iv) maintaining thick liquid flux layer and controlling mould fluid flow to lower the standing wave and level fluctuation.

## Sulphur

The initial sulphur content of the molten iron at Baosteel is ~200 ppm. After hot metal desulphurisation by injection of CaC<sub>2</sub> powder or magnesium based powder, the sulphur decreases to 10–30 ppm. It is important to remove the top slag quickly after desulphurisation in order to decrease sulphur pickup. During the BOF steelmaking process, there is 10–30 ppm sulphur pickup, mainly from lime and scrap. To achieve an ultralow sulphur content, especially for line pipe steels, three desulphurisation methods during the steel refining process have been developed:

- (i) CaO–CaF<sub>2</sub> flux is added to the vacuum chamber through the alloy addition hoppers during RH treatment; slag carryover from the BOF is controlled carefully for these heats, and ladle slag reduction treatment is carried out to decrease the FeO content in the slag before steel desulphurisation; [S] is lowered from 28.4 to 16.2 ppm
- (ii) during RH treatment, after strong deoxidation, CaO–CaF<sub>2</sub> powder is injected into the molten steel in the ladle by a lance below the up snorkel; [S] can be lowered from 61.9 to 35.8 ppm
- (iii) desulphurisation can be achieved at the LF by optimising argon blowing to obtain a suitable emulsification condition, improving the reaction between slag and molten steel; [S] can be lowered from 67.0 to 8.7 ppm. This method can lower the sulphur below 10 ppm, so is currently used for the production of ultraclean line pipe steel. It should be noted that the MgO–CaO refractory lining and tundish flux may also remove some sulphur by the following reaction



## Phosphorus

Five different processing routes are used to achieve low phosphorus steel at Baosteel:

**Table 6 Impurity content of line pipe steel and interstitial free (IF) steel achieved at Baosteel, ppm**

Year	Line pipe steel					IF steel		
	[S]	[P]	TO	[N]	[H]	[C]	[N]	TO
1996	32	134	35	47	2	50	24	50
1999	16	89	24	30	2	23	16	28
2003	9	54	16	30	1.5	16	15	19
2004	4.8	35.0	15.8	29.0	1.0	...	...	...

- (i) de-Si, de-P and de-S at hot metal treatment, followed by BOF steelmaking with a small slag content, lowering [P] to 120 ppm
- (ii) de-S at hot metal treatment, then the BOF process with a large slag content, lowering [P] to 100 ppm
- (iii) de-Si, de-P and de-S at hot metal treatment, followed by BOF steelmaking with a large slag content (slag content index 1.0), lowering [P] to 66 ppm
- (iv) de-P at hot metal treatment, followed by BOF steelmaking with a large slag content (slag content index 0.6), lowering [P] to 58 ppm
- (v) double BOF steelmaking process, achieving 20 ppm [P] in the steel.

The control of impurity elements at Baosteel has improved considerably during the past 15 years, as indicated in Table 6. Baosteel steel can now achieve TO<16 ppm, [S]<5 ppm, [P]<35 ppm, [N]<29 ppm, [H]<1 ppm in line pipe steel, and [C]<16 ppm, TO<19 ppm, [N]<15 ppm in IF steel. Currently, [S]+[P]+TO+[N]+[H] in line pipe steel can be maintained below 85.5 ppm, and [C]+TO+[N] in IF steel can be kept below 50 ppm. Figure 20 shows example distributions of TO, sulphur, phosphorus and carbon along the thickness of an ultraclean steel slab produced in 1997. There is a slight increase in impurities towards the inside radius, owing to inclusion flotation and a very slight centreline segregation.

## Conclusions

1. Techniques to improve steel cleanliness at Baosteel include ladle slag reduction treatment to lower FeO and MnO in the ladle slag to below 5% before steel refining, suitable CaSi wire injection in the ladle, ladle slag detection during pouring, development of a CaO based basic tundish flux, optimisation of flow control devices in the tundish and optimisation of mould flow to avoid mould slag entrainment.
2. Inclusions concentrate mostly within 20 mm of the slab surface. Some slabs experience occasional accumulation at one-quarter to one-half slab thickness from the inner radius, mainly induced by the entrapment of released clogged materials from the SEN during ladle exchanges.
3. Castability has been improved by an improvement of steel cleanliness, the use of optimal calcium treatment to prevent nozzle clogging and application of a breakout prediction system at the caster.
4. Currently, the impurity elements in steel can be controlled to TO<16 ppm, [S]<5 ppm, [P]<35 ppm, [N]<29 ppm, [H]<1 ppm for line pipe steels, and [C]<16 ppm, TO<19 ppm, [N]<15 ppm for IF steels.

## References

1. K. W. Lange: *Int. Mater. Rev.*, 1988, **33**, 53–89.
2. W. B. Morrison: *Ironmaking Steelmaking*, 1989, **16**, 123–130.
3. L. Zhang and B. G. Thomas: *ISIJ Int.*, 2003, **43**, 271–291.
4. A. W. Cramb: in 'Impurities in engineered materials: impact, reliability and control', (ed. C. L. Briant), 49–89; 1999, New York, Marcel Dekker.
5. R. Kiessling: *Met. Sci.*, 1980, **15**, 161–172.
6. N. A. McPherson and A. McLean: 'Continuous casting', Vol. 7, 'Tundish to mould transfer operations'; 1992, Warrendale, PA, ISS.
7. D. Mu and L. Holappa: 'Production of clean steel: literature survey', Report no. PB93–179471/XAB, Gov. Rep. Announce. Index (USA), 1993, 44.

8. Q. Zheng, Z. Chen and L. Zhu: Proc. 13th CSM Annu. Steelmaking Conf., Kunming, China, 2004, Chinese Society for Metals.
9. K. Larsen and R. J. Fruehan: *Iron Steelmaker (ISS Trans.)*, 1991, **12**, 125–132.
10. P. Andrzejewski and K.-U. Kohler: *ISS Steelmaking Conf. Proc.*, 1990, **73**, 41–42.
11. K. Sasai and Y. Mizukami: *ISIJ Int.*, 2000, **40**, 40–47.
12. N. Bannenberg and K. Harste: *Rév. Métall., Cah. Inf. Tech.*, 1993, **90**, 71–76.