SECOND INTERNATIONAL
SLAG VALORISATION SYMPOSIUM
THE TRANSITION TO SUSTAINABLE MATERIALS MANAGEMENT

Recent progress of hot stage processing for steelmaking slags in China considering stability and heat recovery

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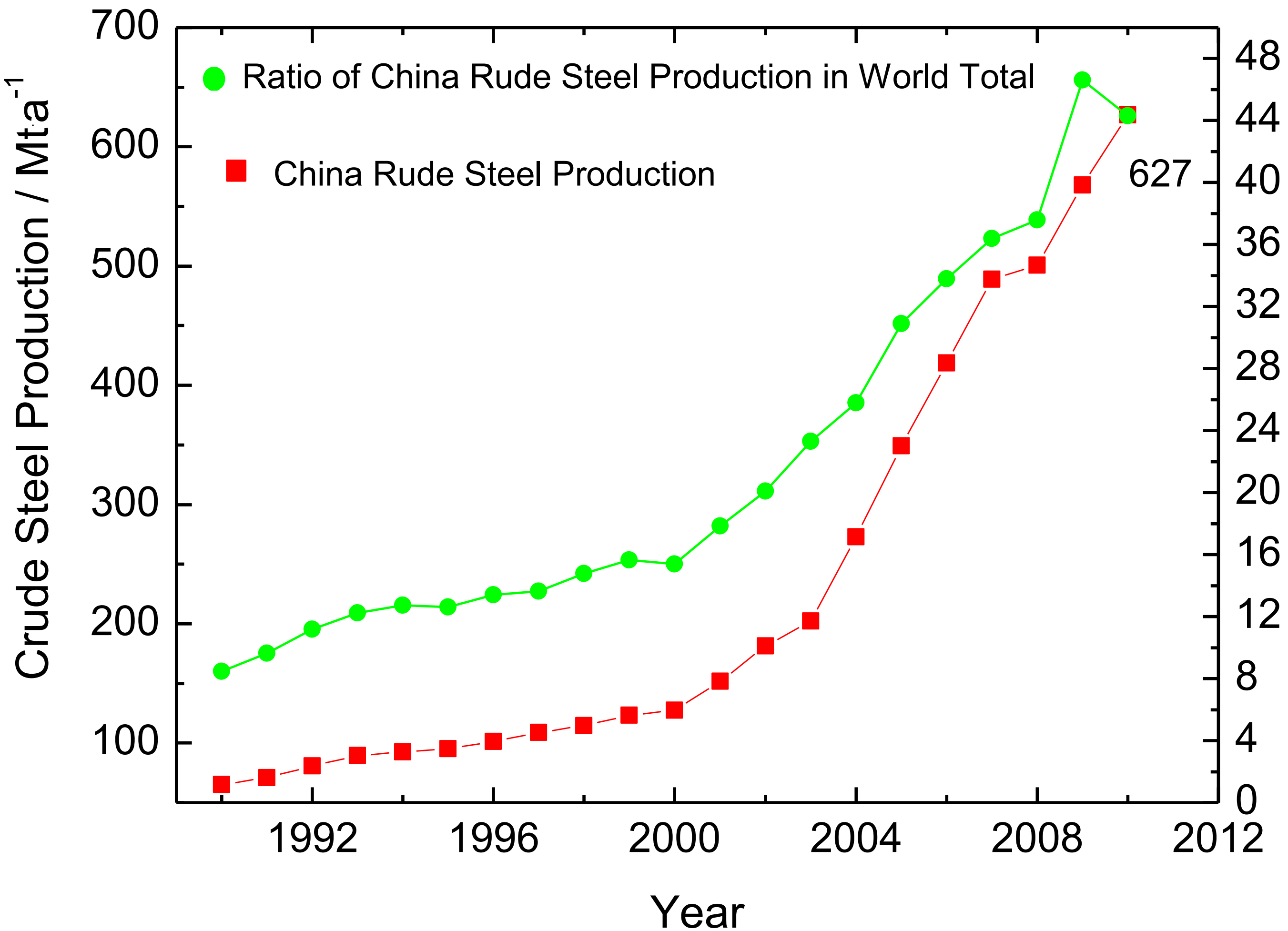
Contents


CHINA
Wuhan


Ratio of China Rude Steel Production in World Total
China Rude Steel Production
627
Crude Steel Production / Mt·a-1
Year
700
600
500
400
300
200
100
48
44
40
36
32
28
24
20
16
12
8
4
0
1992
1996
2000
2004
2008
2012

- In 2005, the total waste heat energy of China's steel industry was 288 kgCE (kilogram of coal equivalent) per tonne of steel. The average recovery ratio was less than 26%.
- Furthermore, the recovery ratio of sensible heat in all kinds of molten slags was only 1.6%.
- In 2009, the total quantity of steelmaking slag was 90 million tonnes in China.
- In 2010, the total quantity of steelmaking slag was 99 million tonnes in China.

- Introduction
- **Treating and heat recovery system for steelmaking slag**
- Dry treating method based on composition modification
- Fundamental Studies
- Conclusions

- **The current hot stage processing of BOF slags**
  - ***Pyrolytic Self-slaking proces***
  - ***Baosteel's Slag Short Flow (BSSF)***
  - ***Instantaneous slag chill process (ISC)***
  - ***Water-granulation process***
  - ***Wheel-granulation process*** (HK)

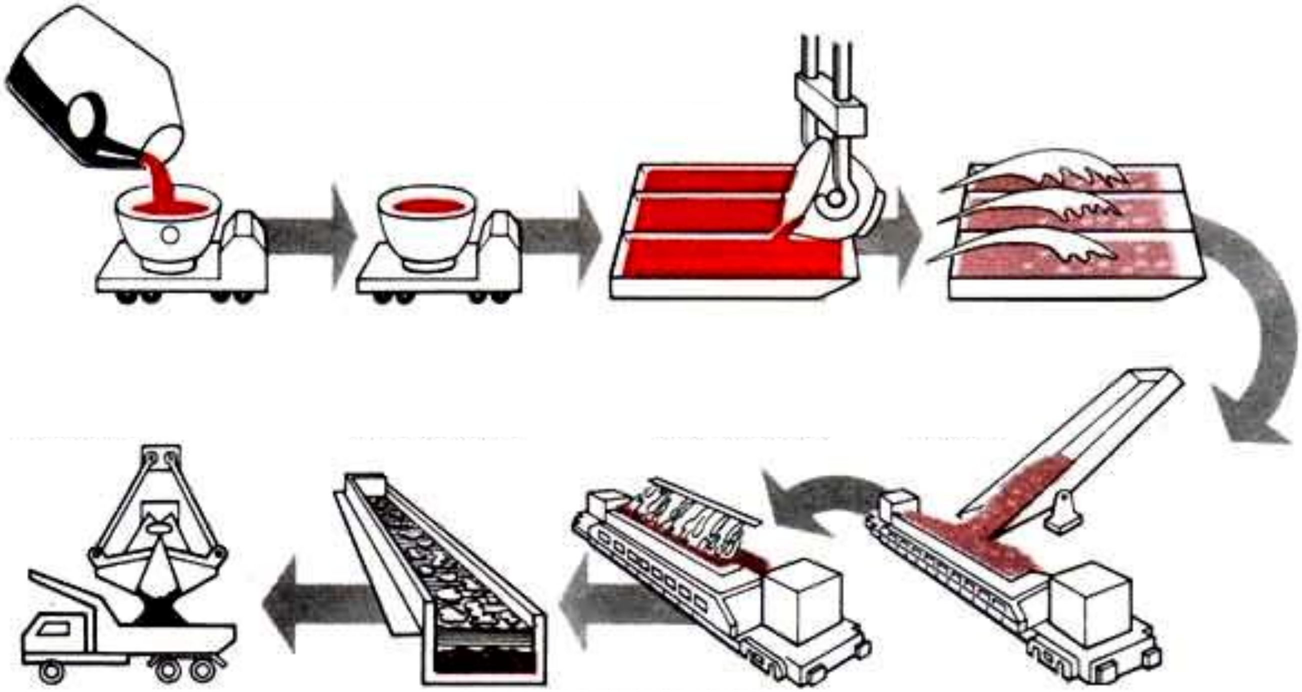
Pyrolytic Self-slaking proces

- The hot slag within a temperature range of 300~800° C is poured into a tank with a cover, while water is sprayed into the tank and thus steam will be generated that reacts with the free lime and magnesia in the slag.

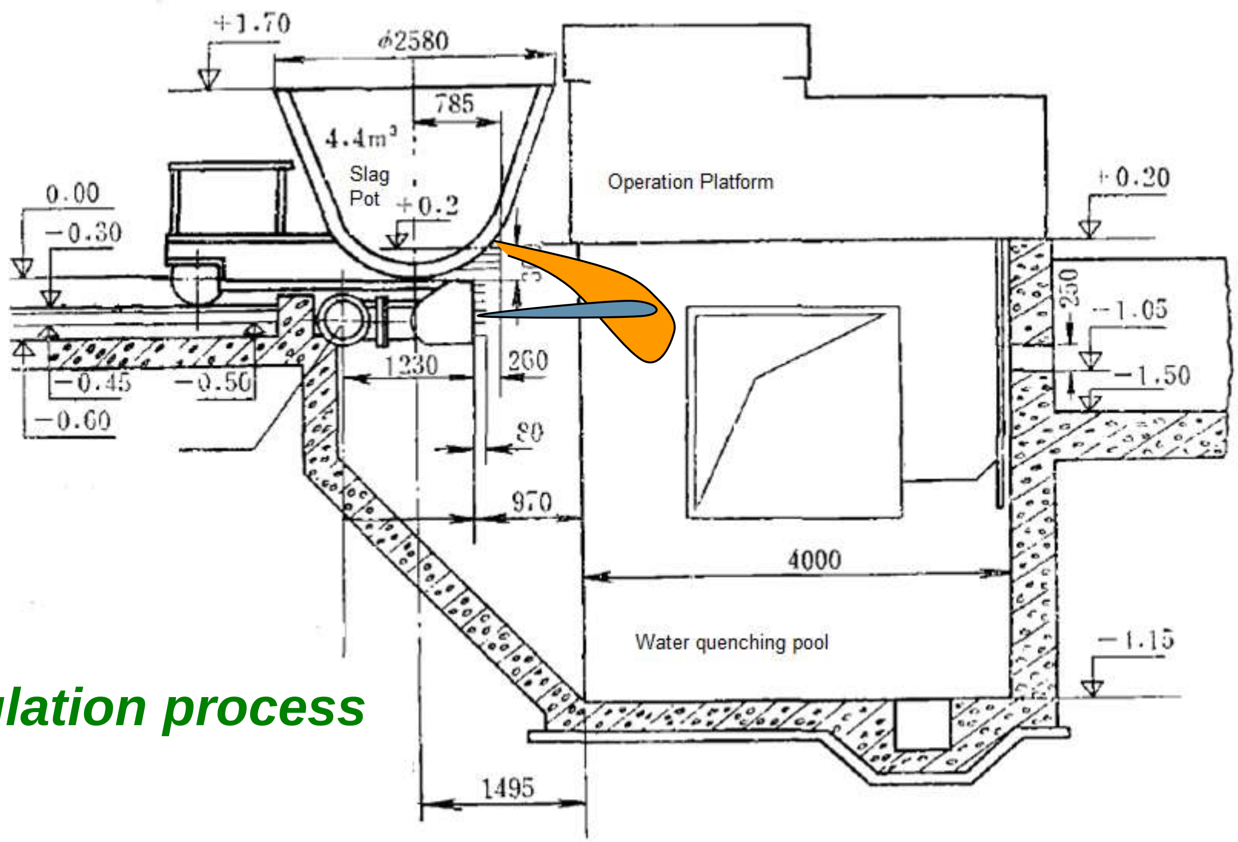
Tiantie：
600,000 tons /a
for 2×180 t BOF

Shaogang：
500,000 tons /a

Instantaneous slag chill process (ISC)



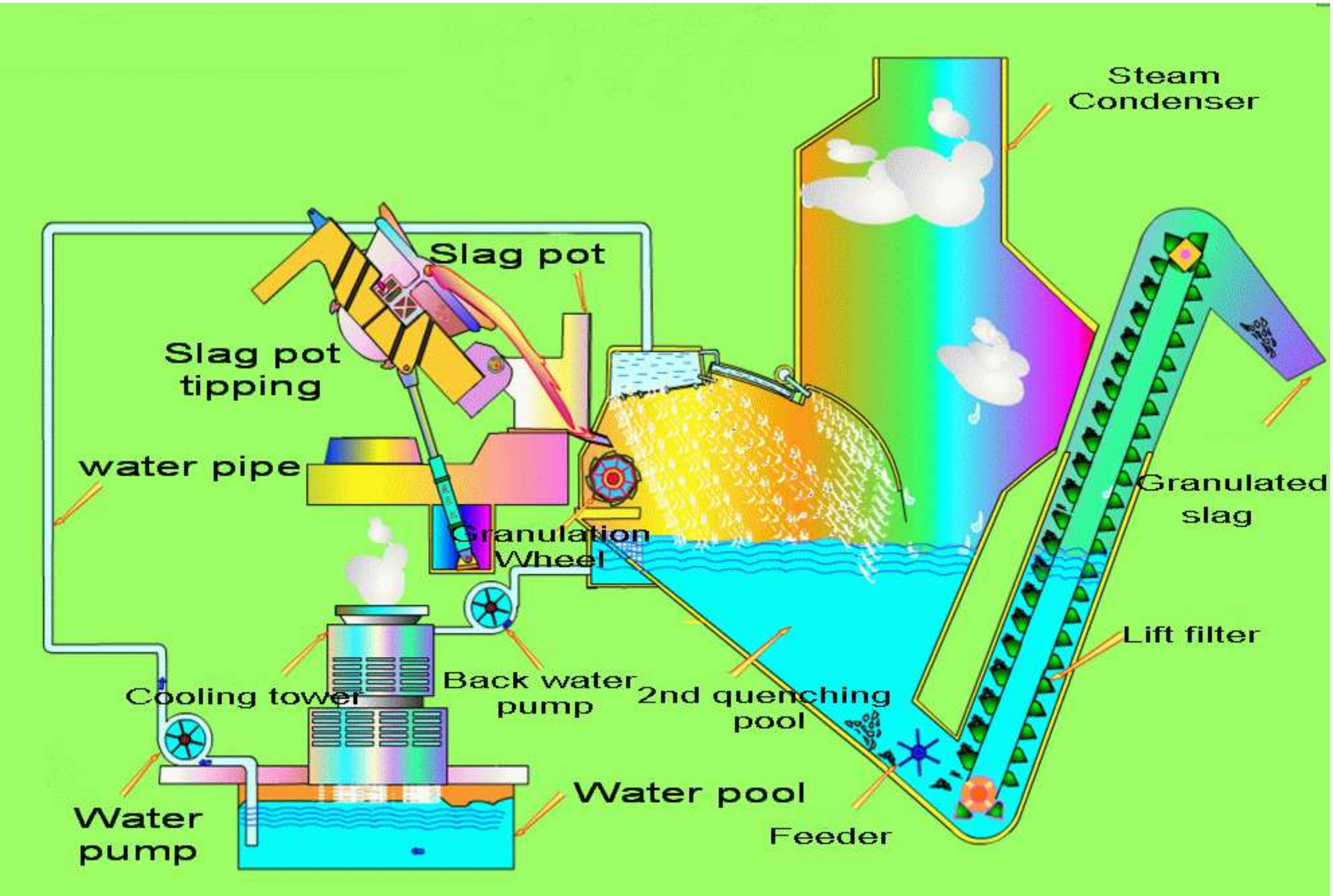
Invented by Nippon Steel and imported by Baosteel in 1980s



Water-granulation process

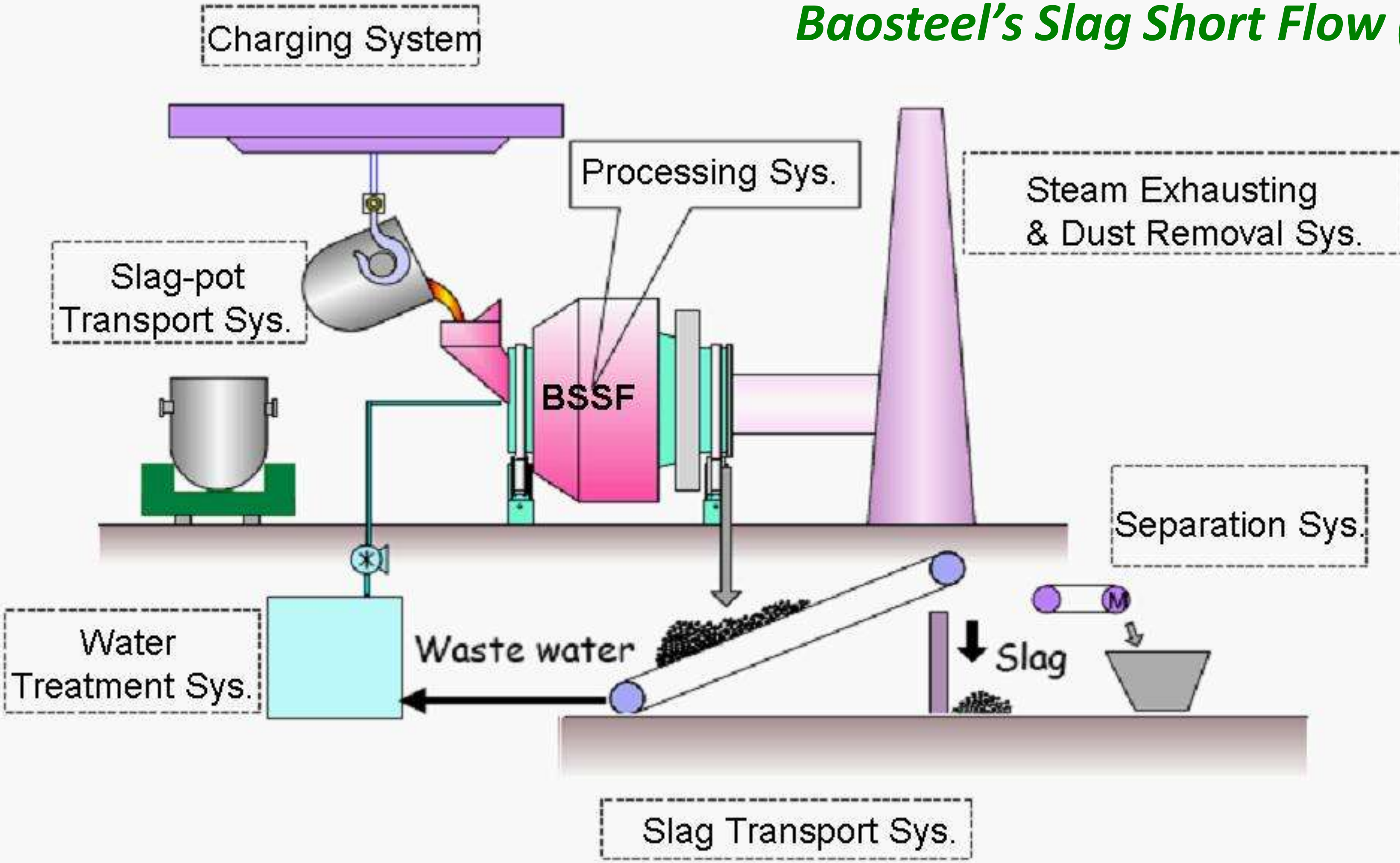
Jinan Steel has been using this process for BOF slag granulation since 1978 for their 25 ton BOF. To avoid explosion, the flow rate of quenching water and molten slag must be well controlled.

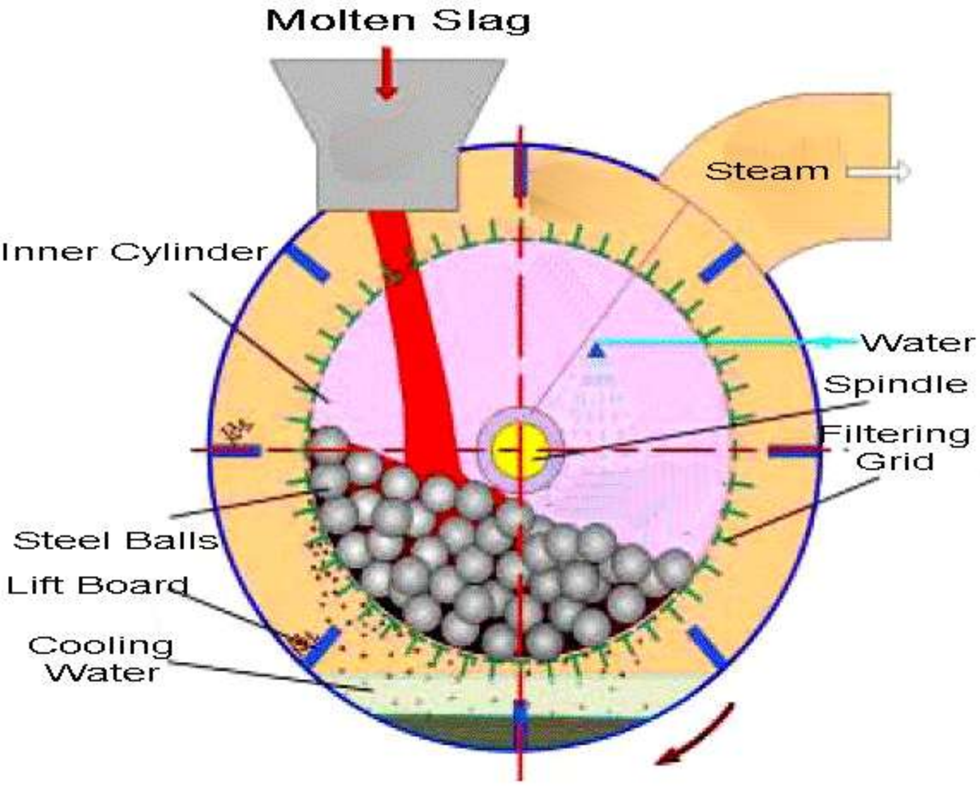
Wheel-granulation process (HK)

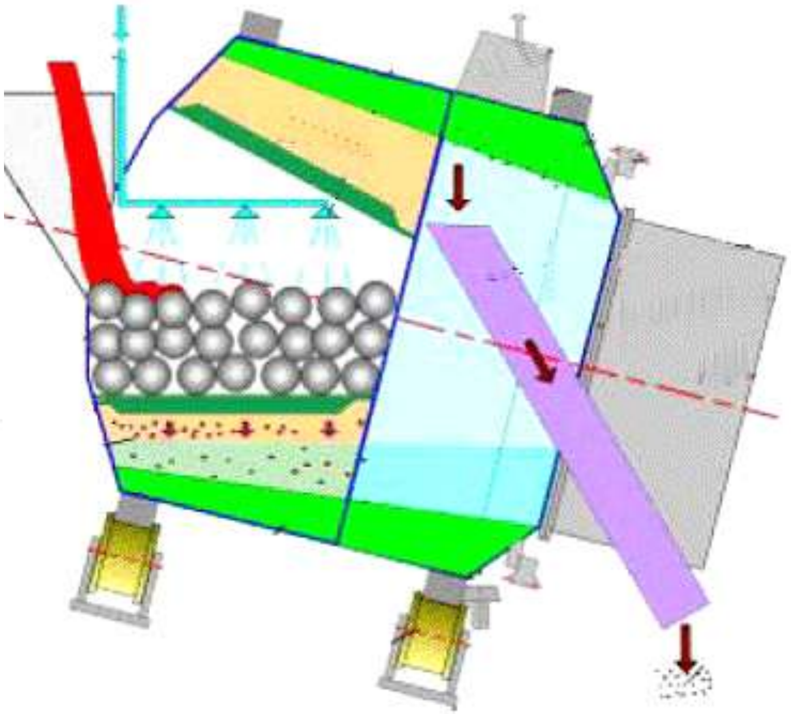


HK process was first applied in Benxi Steel in 2004 for 3×120t and 3×150t BOF. In total 4 units were built. In 2006, Liuzhou Steel built 2 units for their 3×100t BOF.

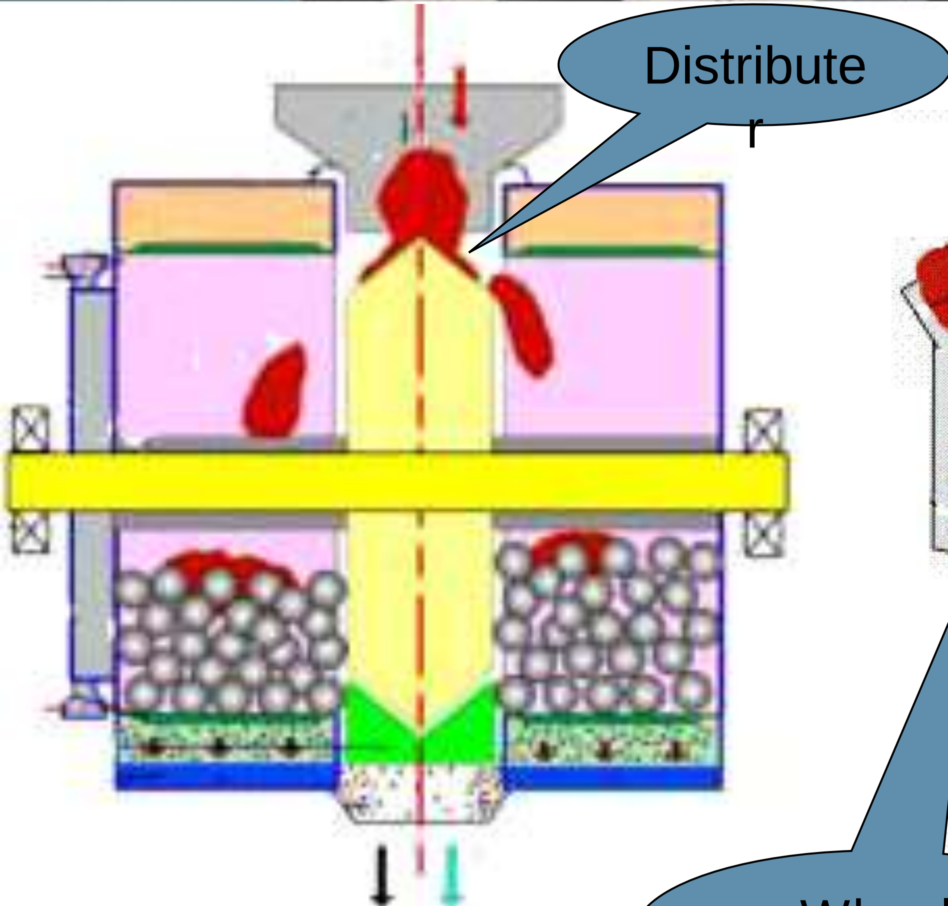
Baosteel's Slag Short Flow (BSSF)



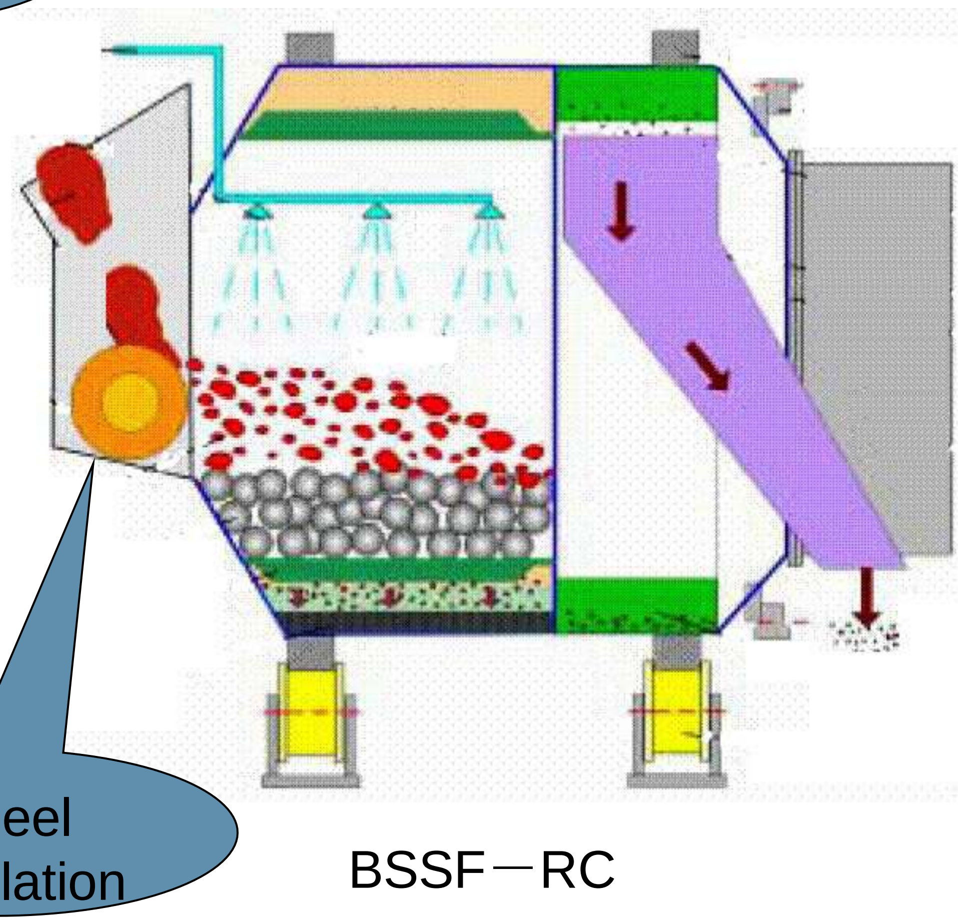

Molten Slag
Steam
Inner Cylinder
Water
Spindle
Filtering Grid
Steel Balls
Lift Board
Cooling Water



BSSF-A



BSSF—B



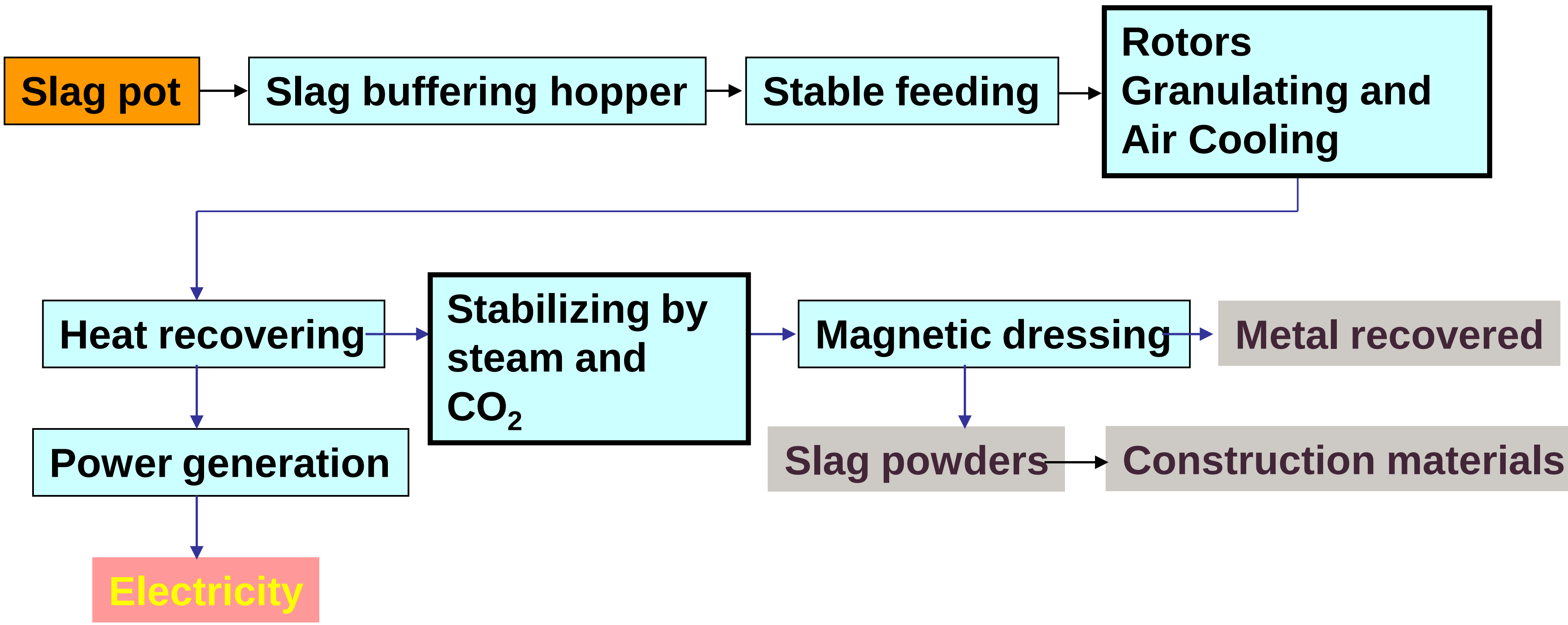
BSSF—RC

Comparison of steelmaking slag granulation processes

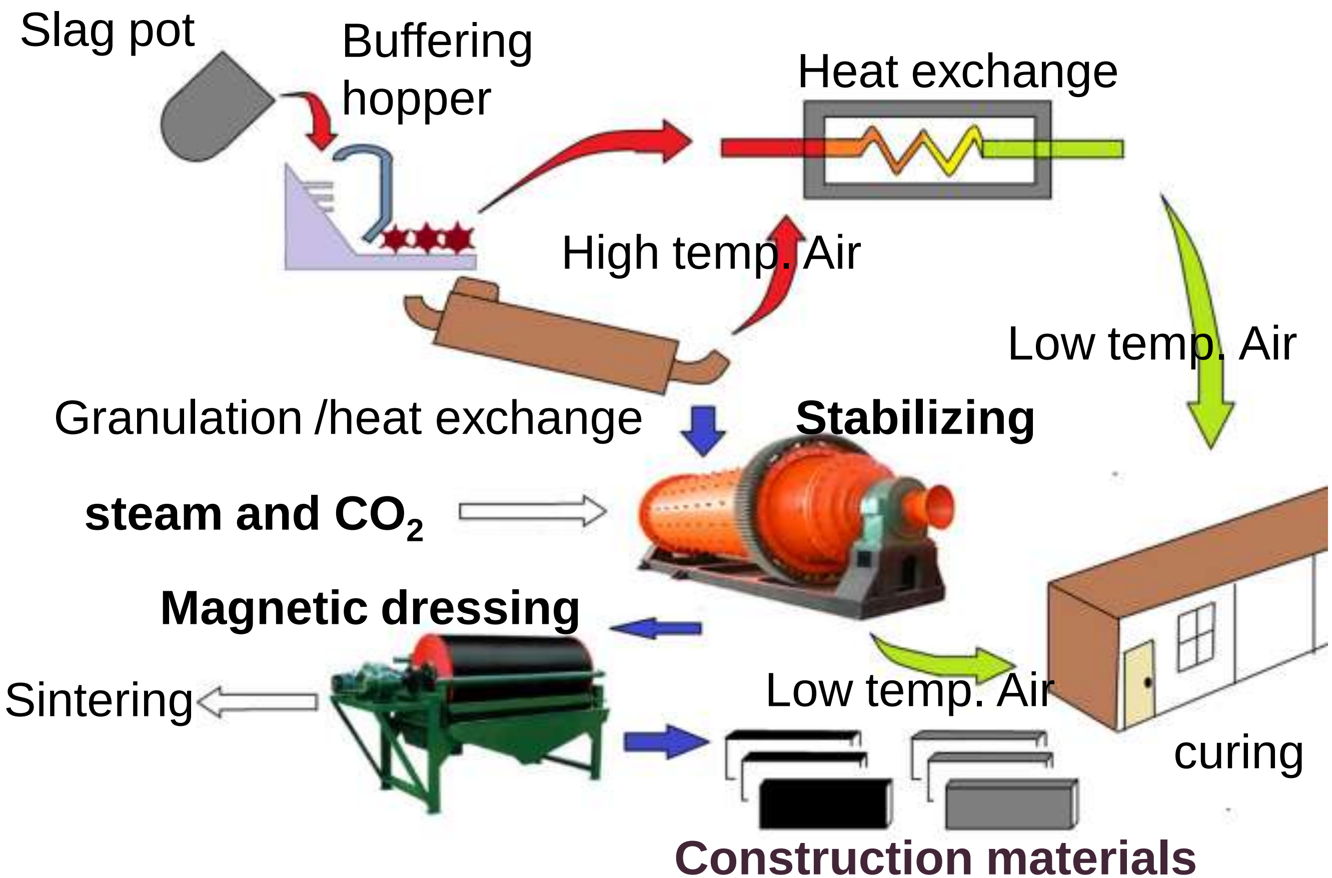
Process	pyrolytic Self-slaking	Air -granulation	Water -granulation	HK	ISC	BSSF
Suitability for slag	All slag	Low viscosity	Low viscosity	Low viscosity	All slag	All slag
Ratio of process	100%	90%	50%	80~85%	100%	100%
safety	high	high	low	low	Relative high	high
Processing ability	20~40heats/3 days/box	2~2.5t/min	1.5t/min	1.5~3 t/min	0.03t/min/ trolley	1~3 t/min
Processing cycle	≥12 h	1~2 min	5~6min	6~8 min	≥2 h	1~2 min
Size of granulated slag	≤10 mm, ≥60%	< 6 mm	≤5 mm, ≥90%	≤12.5 mm, ≥95%	≤300 mm	≤19 mm, ≥90%
Water/Slag ratio (t/t slag)	0.25~0.6	-	10:1	3:1	~0.3:1	1:1
Pressure of media (MPa)	0.3	0.35~0.6	>0.25	0.3	-	0.3
Water supply (t/h)	20	100 circulation	624 circulation	430~480 circulation	circulation	100~180 circulation
Environm.impact	Steam, dust emission	100 dB Noise	Steam emission	Steam emission	Steam emission	Steam emission

- For BOF slag treatment, above mentioned pyrolytic self-slaking, HK, and BSSF processes are being accepted.
- No process considered the heat recovery from molten slag during granulation processes.
- Large scale application of stabilised steel slag powder in construction is a good way for steel slag valorisation.
- The practical feasibility, applicable in large scale, low cost is very important for slag valorisation processes.

Treating and heat recovery system for steelmaking slag in Shougang Group



- Four key problem to be solved:
  - Flexibility to various slag properties;
  - Interrupting input and continuous output of slag;
  - Continuous and stable heat exchange with hot slag;
  - Fast stabilisation of free lime.



- Currently, a testing system for steelmaking slag treatment and energy recovery is being built in the Shougang Group.
- It has the capacity to treat 1 million tonne of slag per year.

Fast stabilisation of free lime

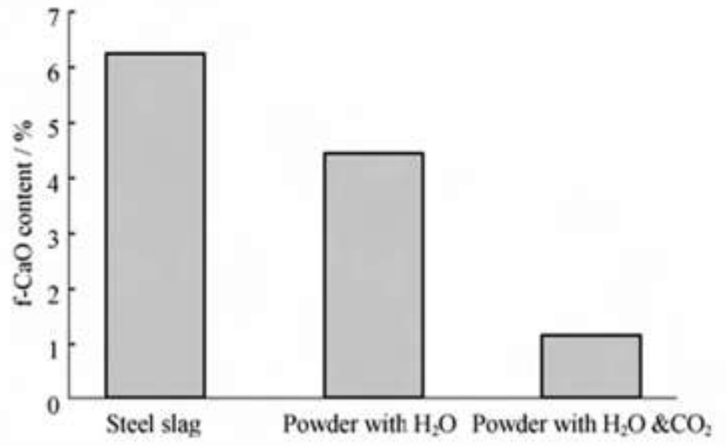


Fig. Effect of 1 h dry ball milling on the content of f-CaO

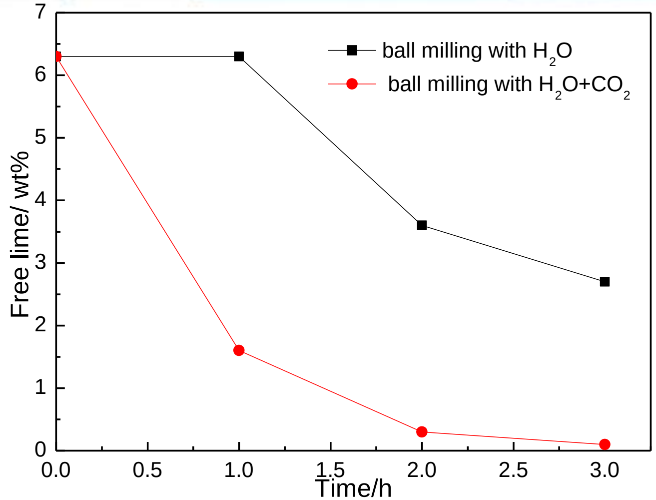


Fig. Effect of wet ball milling on the content of f-CaO

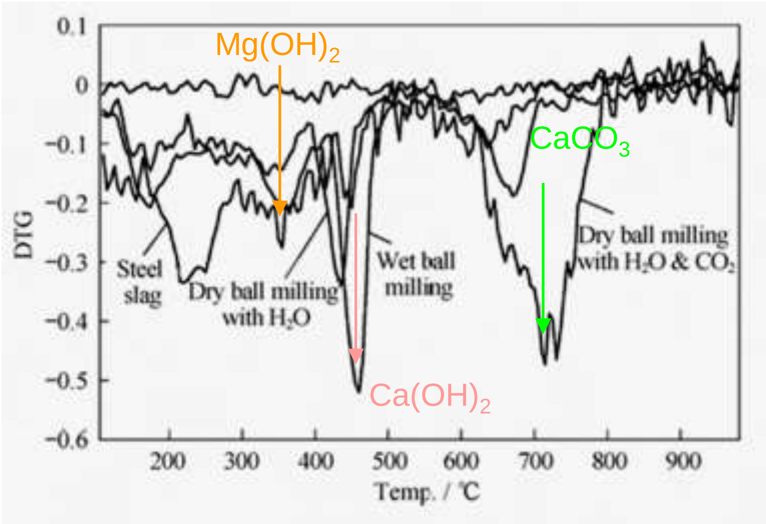


Fig. DTG curves of steel slag after 1 h dry ball milling

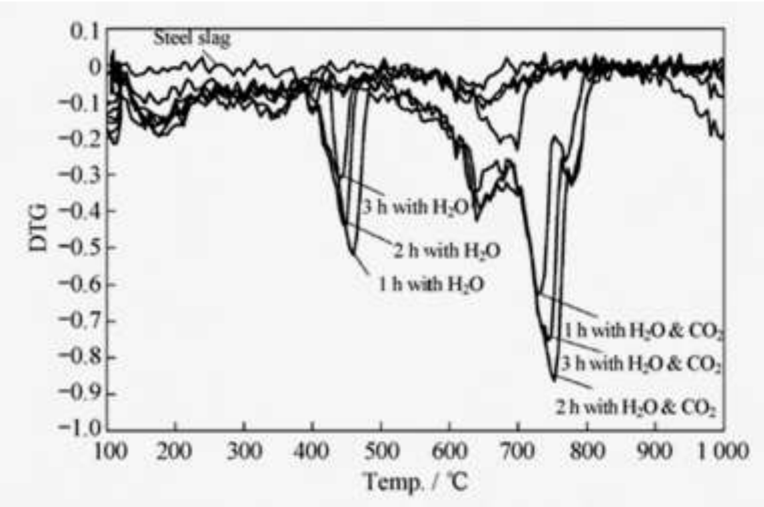


Fig. DTG curves of steel slag after wet ball milling for different time

- The advantages of this technique are:
  - Either a liquid slag with good fluidity or a liquid/solid slag mixture can be treated;
  - There is no danger of explosion as the molten slag does not contact water directly;
  - Gas (air, CO_2 and steam) is only used as heat exchange medium and lime stabiliser but not as granulating energy, thereby lowering the energy consumption;
  - The heat energy of molten slag can be recovered efficiently and slag can be stabilised quickly, the metal can be recycled and the tailings can be utilised.

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Dry treating method based on steelmaking slag composition modification

- The Wuhan Research Institute of Metallurgical Construction developed this slag granulation method considering that the conventionally treated slag cannot be fully utilised due to the lower cementitious activity caused by water treatment.
- Process:
  - Homogenising and composition modifying the molten slag;
  - Water quenching and granulation;
  - Dry the granulated slag powders by high temperature steam recovered from water quenching and granulation;
  - Dry magnetic dressing to separate metal;
  - Utilisation of slag powders.

- Reactions may occur during composition modification of slag:

$$4FeO+O_2=2Fe_2O_3$$
$$Fe_2O_3+nCaO=nCaO\cdot Fe_2O_3$$
$$4CaO\cdot FeO+O_2=4CaO\cdot Fe_2O_3$$
$$4CaO\cdot Fe_2O_3+Al_2O_3=4CaO\cdot Al_2O_3\cdot Fe_2O_3\,(C_4AF)$$
$$2CaO+SiO_2=2CaO\cdot SiO_2\,(C_2S)$$
$$2CaO\cdot SiO_2+CaO=3CaO\cdot SiO_2\,(C_3S)$$
$$3CaO+Al_2O_3=3CaO\cdot Al_2O_3\,(C_3A)$$

- The analysis confirmed that the quantity of main high early strength minerals such as C_4AF, C_3A, and C_3S increased, while the quantity of free lime and free magnesia obviously decreased. Hence, the slag after compositional modification becomes a Portland cement clinker with high early strength and stable properties.

Table 1: Separated products of steelmaking slags

Products	Diameter (mm)	T. Fe (wt %)	Magnetic Fe (wt %)	Ratio (%)	Water (%)	Application
Steel powder	< 1	> 50	--	10~14	< 2	Sintering
Steel grain	1~10	> 90	--	3~7	< 1	Steelmaking
Slag powder	< 0.1	--	< 2	68~78	< 2	Construction material
Slag grain	0.1~5	--	< 2	5~15	< 1	

- **The advantages of this process**
  - Continuous production;
  - Small number of processing steps;
  - The investment and space requirements are 30% lower than conventional slag treatment processing;
  - Expanded range of applications. free lime and other unbeneficial components is less than 1%. As the strength of construction materials made of treated slag powders are improved over 40%.

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Fundamental Studies

- National Natural Science Foundation of China (NSFC) project :"Fundamental study on key techniques for the preparation of high value products by utilisation of both heat and slag".
- The process proposed targets the modification of the slag composition by :
  - Carbothermic reduction to reduce iron oxides in the molten slag.
  - Waste refractory materials containing silica and alumina are added into the molten slag to lower the viscosity and adjust the slag composition making it suitable for making glass ceramics.
  - The liquid slag is air granulated and heat can be recovered.
- Component modification of steelmaking slag in an air quenching process to improve grindability was reported.

Table 2: Composition of modification agents and original BOF slag (wt %)

Component	T. Fe	CaO	MgO	Al_2O_3	SiO_2	S	f-CaO	FeO	M-Fe	C
Fly ash	1.53	5.3	0.78	21.53	67.27	0.47	--	--	--	3.59
Mill tailings	15.79	--	--	--	63.42	1.53	--	0.71	--	--
Steel slag	17.28	44.73	8.46	4.6	14.53	0.045	9.54	21	8.45	--

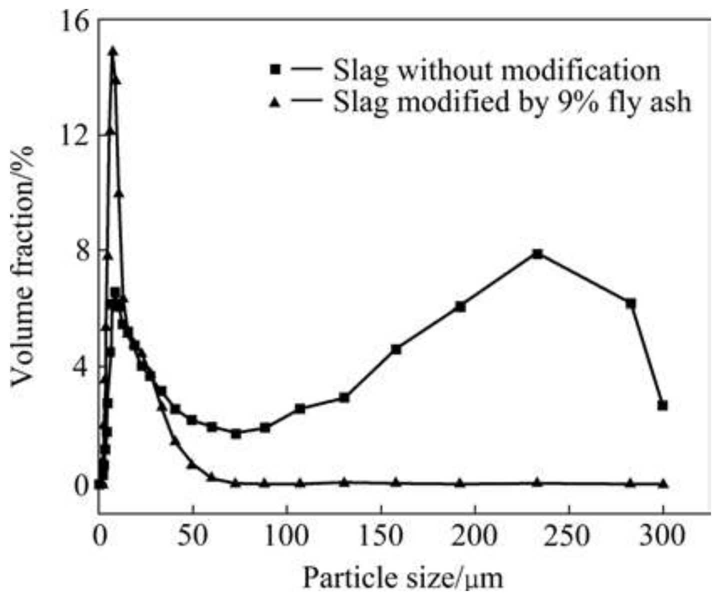


Fig. Particle volume fraction of slag modified by 9% fly ash and original slag

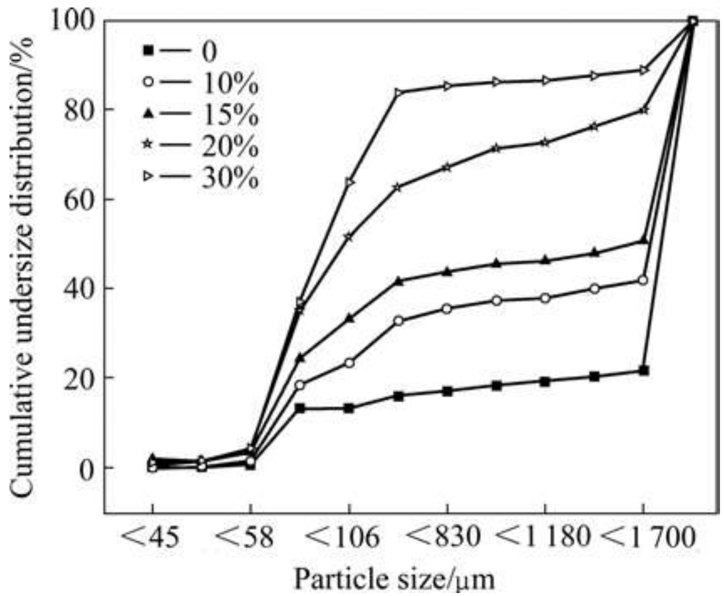


Fig. Cumulative undersize distribution of steel slag with different ratios of fly ash

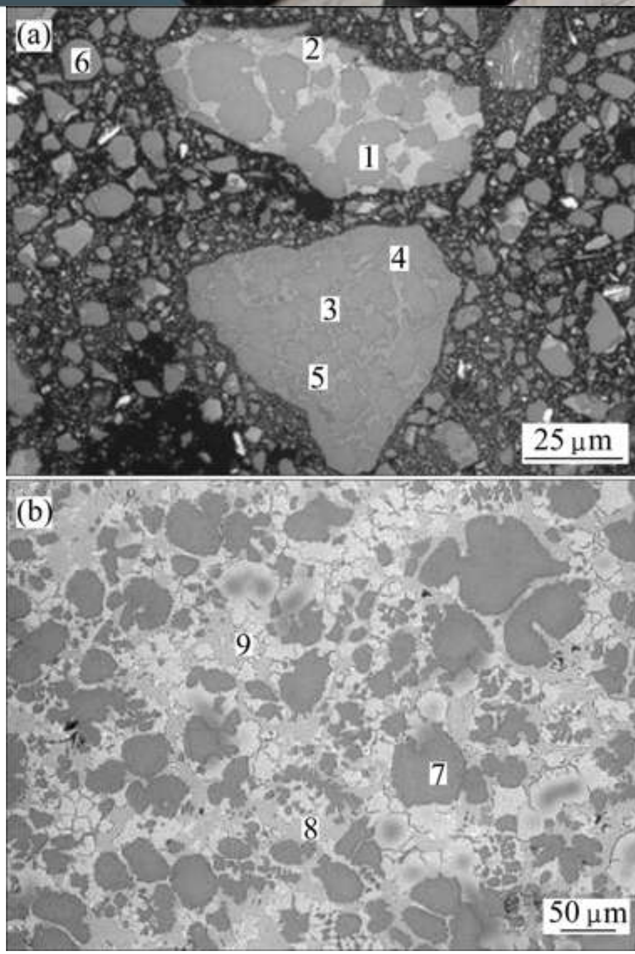


Fig. SEM images of slag without fly ash added: 1, 3, 6—$3CaO \cdot SiO_2$; 2, 4, 5—RO; 7—$CaO \cdot SiO_2$; 8—$CaO \cdot Fe_2O_3$; 9—f-CaO

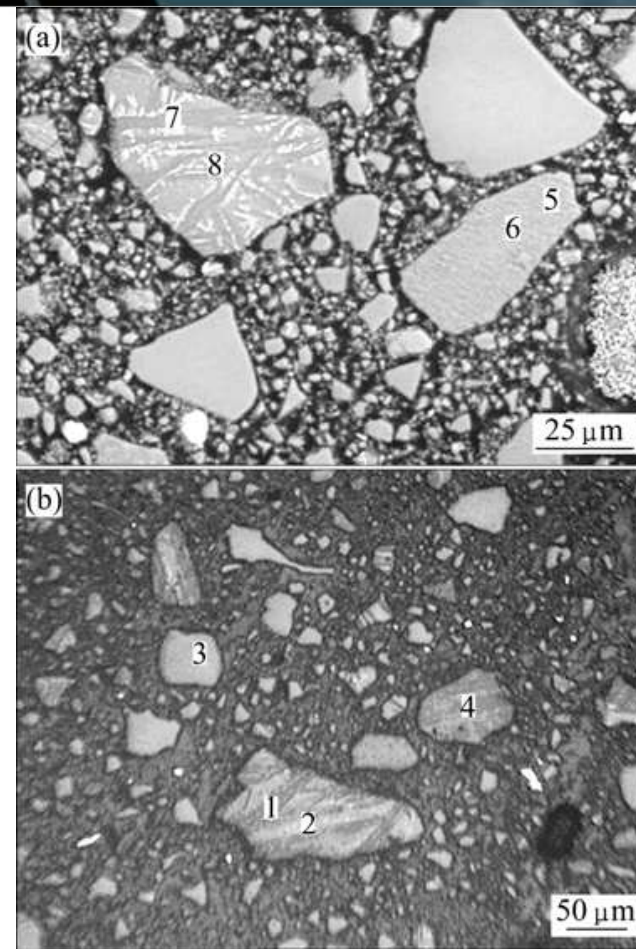
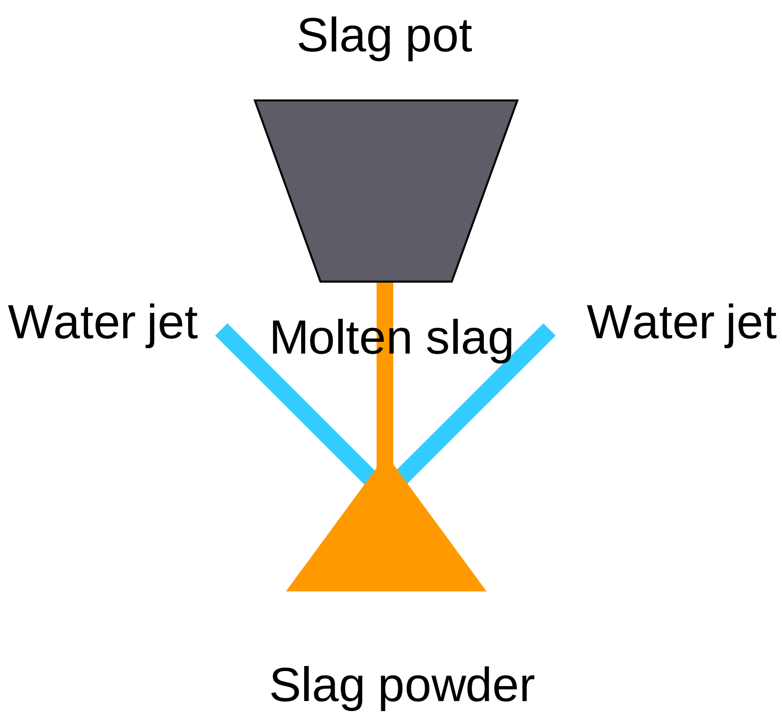


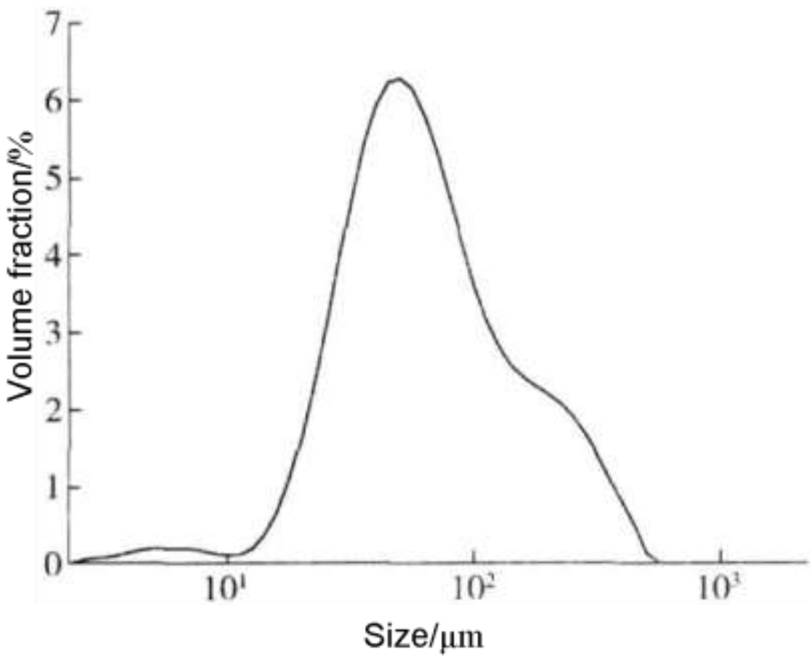
Fig. Micrographs of slag with 5% fly ash added: 1, 2, 3, 4—$CaO \cdot SiO_2$; 5, 7—$2CaO \cdot SiO_2$; 6—$CaO \cdot FeO \cdot SiO_2$; 8—RO

Granularity and reactivity of molten slag quenched and atomised by a high pressure water jet

Experiments about cooling and pulverising the molten steel slag and blast furnace (BF) slag by a high pressure water jet of 8 to 10 MPa were conducted on a self-made slag melting and high pressure water cooling system.



Slag melt jetting by high pressure water stream



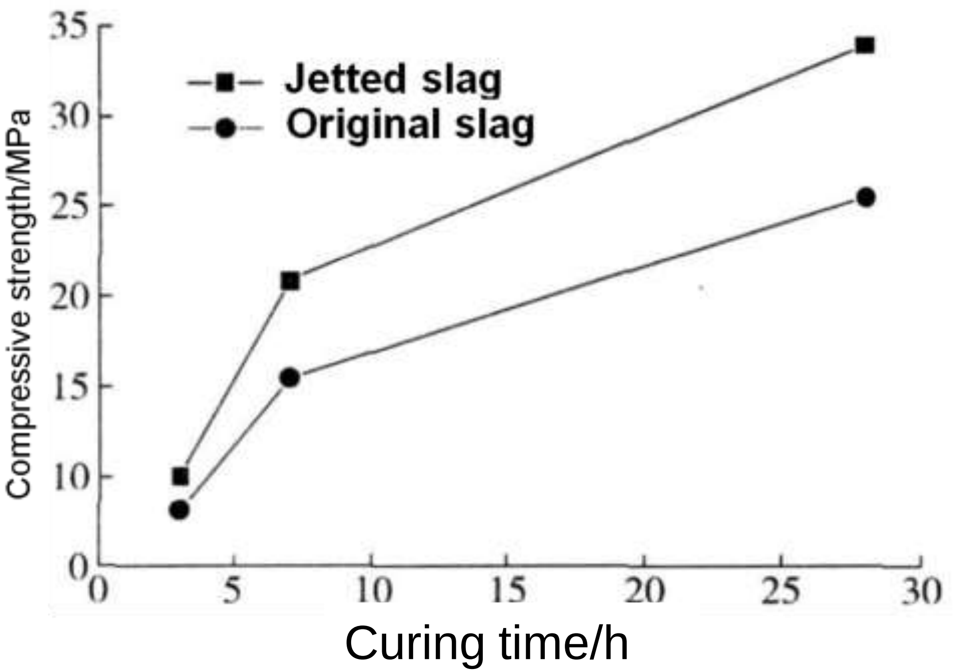


Fig. Particle size distribution of jetted steel slag

Fig. Comparison of compressive strength of cement samples from jetted and original steel slag

- Preparation of glass –ceramics from liquid steel slag
  - 40% EAF slag was melted at 1724 K and then mixed with 60% melting additives (containing silica, alumina and sodium oxide), subsequently heated to 1773 K for 1 hour. Then the modified slag was cast, annealed and transformed to glass–ceramics.

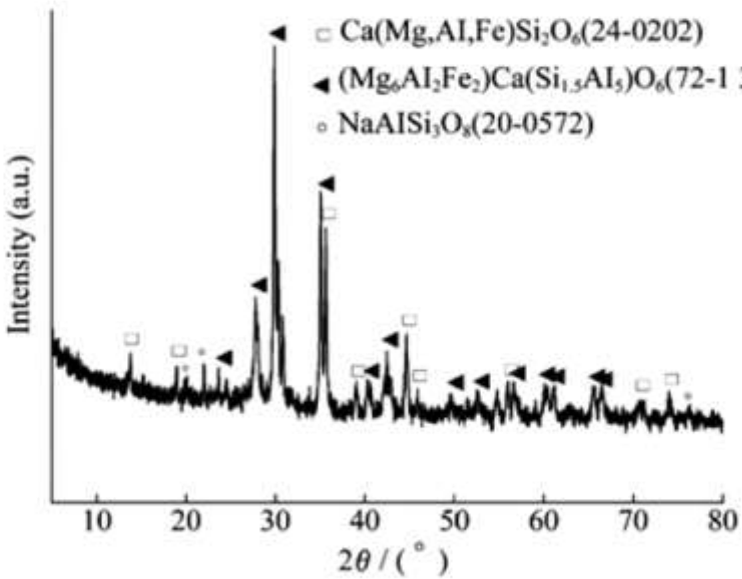


Fig. XRD patterns of glass-ceramics

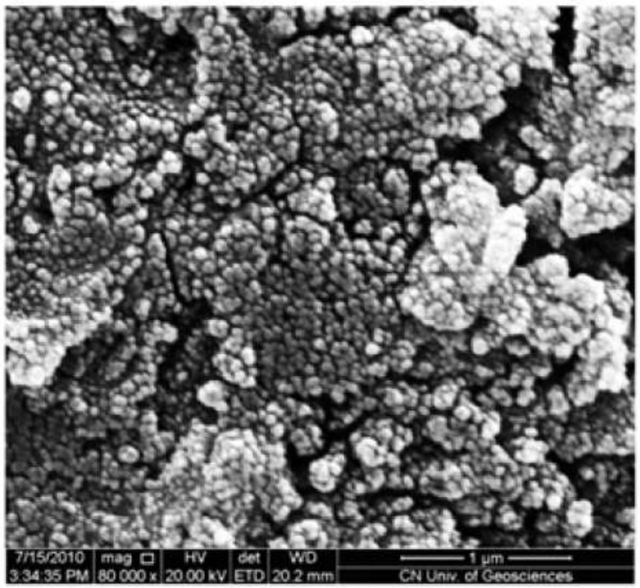


Fig. SEM image of glass-ceramics

- Simulation on heat recovery in dry granulation process of steelmaking slag

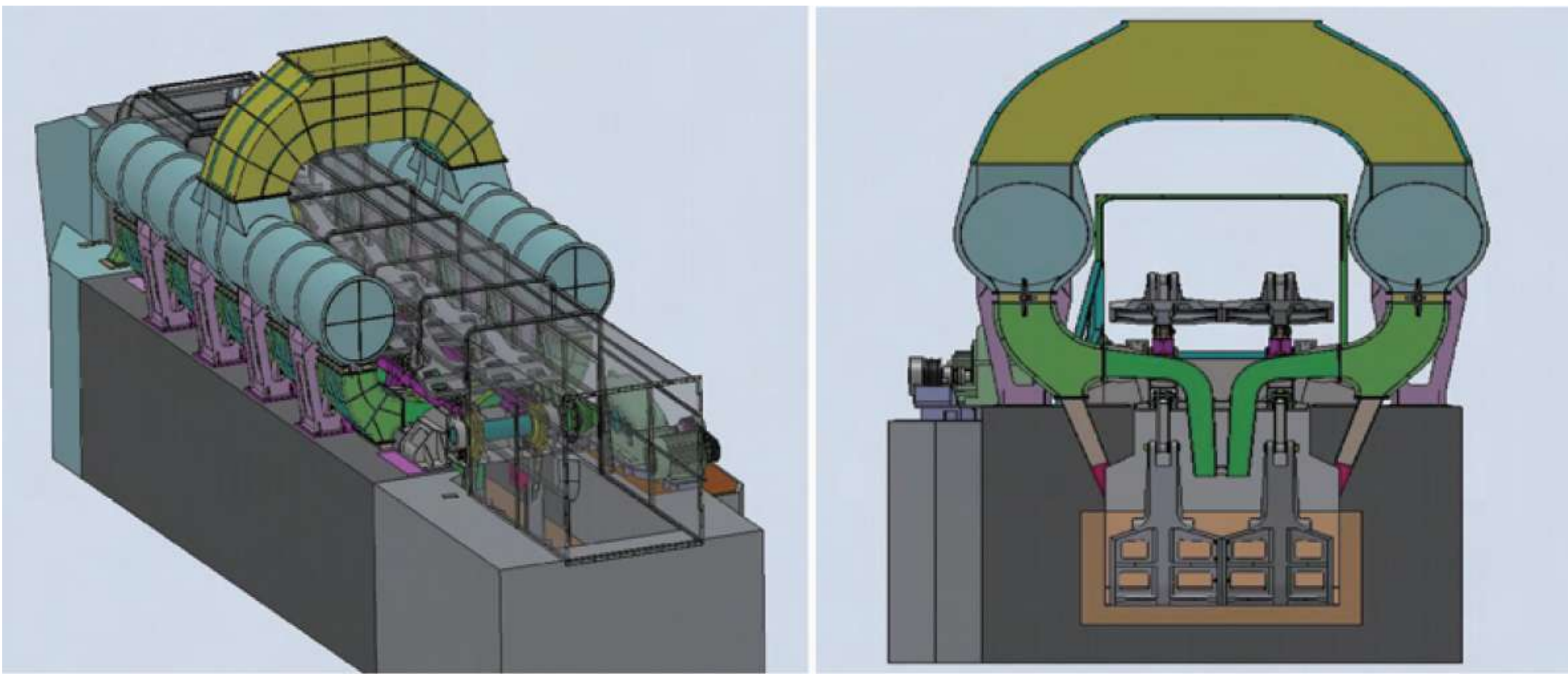


Fig. Schematic diagram of the system of granulation heat exchange

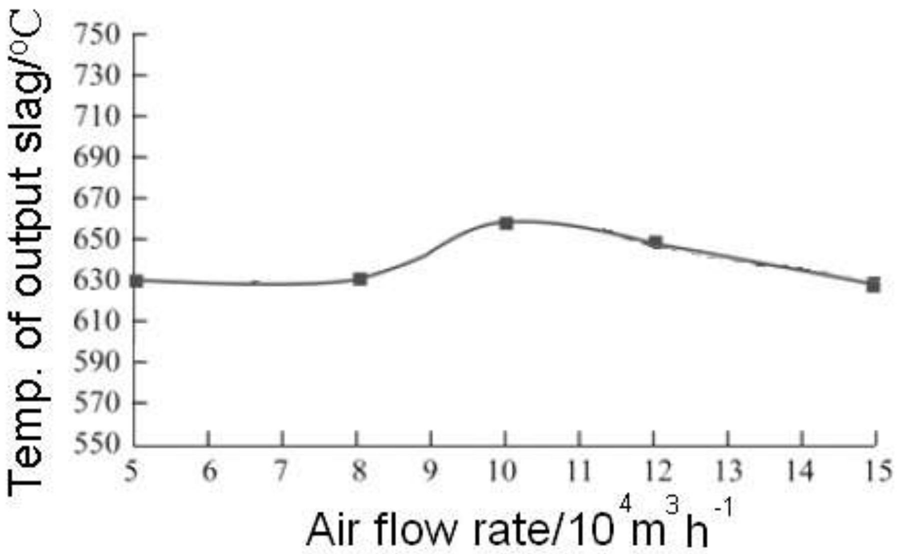


Fig. The average temperature of output slag as a function of the air flow rate

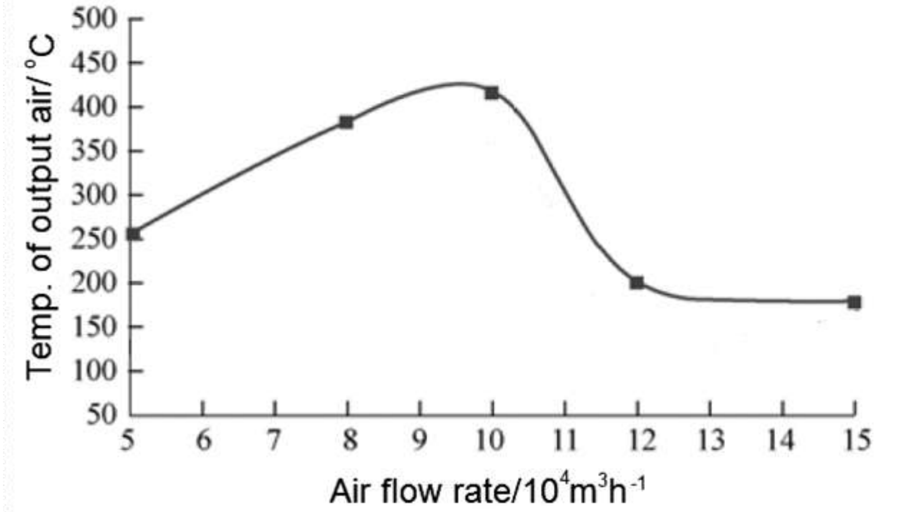


Fig. The average temperature of output air as a function of the air flow rate

- The temperature of output granulated slag will be 900 K if the input slag temperature is 1673 K. The temperature of room temperature blown air was increased to 693 K after heat exchange with molten slag. The flow rate of air in the range of 80000 to 100000 m3/h results in slag cooling and heat recovery efficiently.

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Problems of sensible heat recovery of molten slag

- Problems of sensible heat recovery of molten slag:
  - There are two solid phase: crystal phase and glass, the heat conductivity is different:
    - Liquid slag: 0.1~0.3W/m^2K, Glass: 1~2W/m^2K, Crystal: ~7W/m^2K;
  - Fast granulate to small particles is precondition.
  - Most developed or under developing methods are physical methods based on air, steam or hot water as heat recovering medium; the quality of recovered heat is poor;
  - The energy conversion are multi-steps;
  - **Low exergy efficiency** of sensible heat recovery from molten slag is the key problem.

Conclusions

- According to the pilot-scale experiments and fundamental studies on hot stage steelmaking slag treatment recently carried out in China, heat recovery from molten slag in the slag granulating process must consider the massive application of treated slag products and engineering possibility of the process.
- No matter what process is selected, molten slag with suitable fluidity is essential for smooth and continuous processing. For this reason, slag modification in composition and temperature are necessary in some cases. Slag modification in composition is also a measure to decrease the basicity of slag, enlarge the application areas of steel slag products.
- Completely dry treatment is impossible to eliminate free lime. Therefore, water quenching, steam treatment, or wet milling, carbonating must be included in the process.
- Making use of the sensible heat of molten slag and decreasing the energy input during molten slag treatment should be acceptable instead of net energy recovery.

Thank you for your attention!