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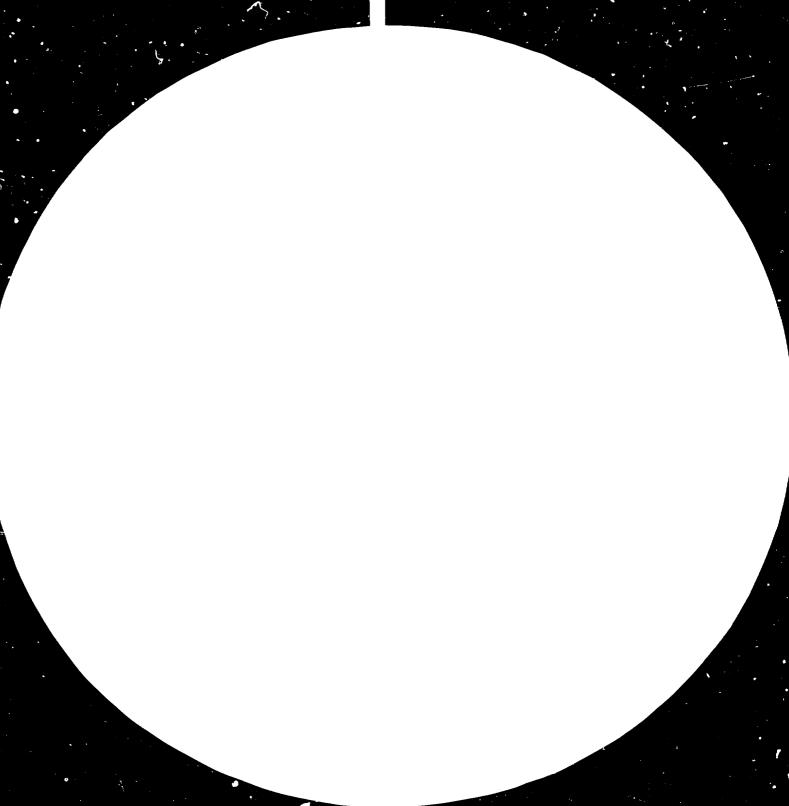
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LD STEEL SLAG-ZEOLITE CEMENT \*

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### Introduction

LD steel slag is an industrial waste, which, in combination with zeolite rock, can be used to produce directly cement without calcination. This procedure for cement production opened up a new way for comprehensive utilization of the abundant resource of steel slag. In this way, a former waste is transformed into a "clinker" of cement and a great deal of energy resources is economized in cement production.

We began in 1970 to study the utilization of the unquenched LD steel slag in cement production.A factory especially designed to produce steel slag cement, The Steel Sag Cemnt Factory of Peking, was set up in 1971, whose present annual output amounts to 70,000 tons of Grade 40G steel slag-zeolite. cement (SZ cement).

Following is a brief description of the production, utilization and proerties of SZ cement.

Mineral Composition and Activity of Steel Slag

Compared with the similar kinds of steel slag in our country, the LD steel slag from the capital Steel Company used in our experiments and production is rich in Ca and Al, intermediate in Mg, and poor in Fe and P (Table 1).

It can be seen from Table 1 that the chemical composition of the steel slag varies in a somewhat wide range. The calculated alkalinity of the steel slag is in the range of 2.5-4.0 with the majority above 3.0.

The mineral constituents in the steel slag are rather complicated. The principal mineral phases are  $C_3S$ ,  $C_2S$  and RO etc. Weaving together to form an interlocking framework, the crystals of  $C_3S$  and mostly tabular, prismatic and hexagonal. Its grain size rainges between 0.1-0.8mm, with the largest crystal amounting to 4 mm. The volume percentage of  $C_3S$  in the steel slag is 30-50 %. As shown in Table 2,C S phase contains a small amount of FeO and MgO.

Date of sampling	No:	\$10 <sub>2</sub>	Al.203	Fe203	FeO	Ca0	MgO	MnO	FCa0	P205	Alkalinity
1976.2	76-3	14.86	7.90	2.79	8.91	52.3	14.7	1	;	0.61	3.5
1976.2	76-0	22.79	4.69	2.39	5.11	50.5	12.7	1	2.45	0.53	2.2
1979.1	79–1	17.14	7.48	13.80	6.49	47.0	11.5	1	2.00	1	2.7
1979.3	79-3	14.7	4.80	5.86	1.31	46.7	8.6		1		3.2
1979.4	79-4	15.45	2.25	10.70	9.78	44.8	9.0	3.5	1	0.53	2.9

Table 1 Chemical Composition of the LD Steel Slag from the Capital Steel Company

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Sample No	Mineral phase	Crystal form	\$10 <sub>2</sub>	Ca0	MgO	A1203	Feg03	MnO
75-20	C <sub>3</sub> S	hexagonal	17.1	67.9	1	7	0.43	7
76-4	c <sub>3</sub> s	elongated tabular	23.6	70.0	/	/	2.19	0.4
76-7	C <sub>3</sub> S	prismatic	21.4	93.0	1	1	1.85	0.4
75-33	c <sub>2</sub> s	elongated tabular	38.6	66.4	3.32	0.19	0.71	0.78
76-3	C <sub>2</sub> S	rhombic	34.3	49.1	1	1	0.14	0.13
76-2(1)	RÖ	elongated tabular	1	e.70	59.5	1	3.00	2.08
76-2(2)	RO	rounded	1	0.42	72.8	1	18.7	1.30
76-3	RO	polyangular	<u> </u>	1.26	24.8	1	47.6	20.40
76-2(2)	RO	polyangular		0.56	84.4	1	16.3	11.70
76-2(2)	RO	polyangular	1	0.70	74.5	1	25.8	1.90
76-2(2)	C <sub>2</sub> F	elongated tabular	/	52.2	1	11.3	27.2	1
76–1	C3MS2	н	38.6	49.6	13.3	1	0.57	0.39
76-1	CZMS		34.3	60.6	8.30	1	0.28	0.65
76-20	FCaO	rounded		109	1	1	5.0	0.19
76-20	F CaO	11	/	41.4	1	/	4.56	).18

Table 2 Electronic Microprobe Analysis Data of the Steel Slag

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Being in the form of elongated plate and rhombus,  $\beta$ -C<sub>2</sub>S phase constitutes about 20-30 % (volume percentage ) of the steel slag and contains also minor Mg0, FeO and MnC. The volume percentage of RO phase is around 20 %. Two modifications of RO phase can be distingushed on the basis of their chemical composition. One consists of essentially MgO or FeO, with minor FeO, MgC and CaO. It is not a pure perclase (MgO) and can not be hyrated to from Mg(OH)<sub>2</sub>. Therefore, it is a harmless constitueent in cement, the other consists of essentially CaO, with minor FeO and MnO and is characteristic of the steel slag. Contrary to the first modification, it can be hyrated to form Ca(OH)<sub>2</sub>, resulting in the poor soundness of the traditional LD steel slag cement.

Although the principal phases  $C_3S$  and  $C_2S$  in the LD steel slag from the Capital Steel Company resemble closely that in clinker and suitable for the direct production of cement.The activity of LD steel slag is lower than that of cement, because the grain size of  $C_3S$  and  $C_2S$  crystals crystallizing directly from the melt at very high temperature is much larger than that in clinker.

### Role of Zeolite in SZ cement

The zeolite rock used in the production of S2 cement is composed mainly of clinoptiloite and mordenite.Zeolite contains a certain amount of active silica and alumina, which can be combined under the alkaline condition with the free CaO in the steel slag and hence eliminated the factor causing poor soundness of the traditional steel slag cement.Through the experiments and production conduced by us for the last three years, zeolite rock has proved to be a superior active mixed material.It is highly effective and inexpensive.

In our opinion, a series of chemical reactions may very likely take place in the steel slag cement after the addition of zeolite rock.At first,Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> are removed or disso-

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No	Fineness	Soundness	Setting Hr:M		Tensile strength Kg/om <sup>2</sup>			Compressive strength Kg/cm <sup>2</sup>			
			initial set	final set	3d	7đ	28d	3d	7d	28d	
KSC-1	6.8	qualified	2:20	8:10	16.5	20.9	29.6	143	306	477	
KSC-9	8.0	17	0:45	8:10	14.1	23.6	34.3	146	331	508	
0S2-5	7.6	10	/	5:45	16.9	22.0	31.7	215	314	560	

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Table 3 Physical Properties of SZ Coment

Table 4 The Heat of Hydration of S2 Cement

Type of cement	Heat of hydration of cement						
	3d	7d					
400* SZcement	31.9	39.1					
и	30.3	41.8					
н	28.5	40.0					
400-500* Pozzolanic cement	30-40	<b>4</b> 0~50					
Portland cement	63.6	70.4					

ciated from the crystal framework of zeolite. Then the hydration product of the free CaO present in the cement is combined with the dissociated silica. Therefore, we call the above process a "mechanism of multistage chemical reactions consisting of removement of  $Al_2O_3$  and dissociated  $SiC_2$  from zeolite and combination of  $Ca(OH)_2$  (with the dissociated  $SiO_2$ )."

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The combination of the hydration product of free CaO in the cement with the SiO<sub>2</sub> released from zeolite greatly improve both the soundness and the strength of the steel slag-zeolite cement. This explains why the properties of the steel slag-zeolite cement is superior to that of the traditional steel slag cement.

Properties of the LD steel slag-zeolite cement

SZ cement can be manufactured directly from LD steel slag, zeolite rock and other active materials. Its physical properties are listed in Table 3.

As shown in Table 3, both fineness and soundness as well as setting time and strength are in accord with the requirements specified on the National Standard of PRC (GB). Its compressive strength reached 450-500 Kg/cm<sup>2</sup> by the end of 28 days.

The hydration heat of SZ cement is lower than that of portland cement. It can therefore be suitably used in engineering properties involving tremendous quantity of concrete pouring, such as irrigation engineering, etc.

By using the standard ASTM procedure, the SZ cement was cured at 20 atm.for 3hours and its expansion coefficient was then measured.The experiment results (Table 5) show that autoclave property is fairly good.

The corrosion resistance of the S2 cement is much better than that of ordinary cement. It can especially stand the corrosion of sulphate (Table 6).

#### Summary

Ten years have elspsed since we began to produce the steel

Table 5 Results of autoclave test

Type of coment	rate of expa	nsion
-	after steam test	after autoclave test
SZ cement	0.103	0.063
SZ cement	0.133	0.090
SS cement	0.042	0.152

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Table 6 Results of sulphates as corrosive agents

No	H <sub>2</sub> O Kg/cm <sup>2</sup>			cm <sup>2</sup>	MgSO <sub>4</sub> Kg/cm <sup>2</sup>				Na2SO4 Kg/om <sup>2</sup>			
	30a	90a	18Ud	кс <sub>6</sub>	30a	90d	180d	<b>K</b> C <sub>6</sub>	30d	90 <b>d</b>	180d	кс <sup>6</sup>
B102	53.5	57.8	61.2	1	55.0	56,8	63.3	1.05	56.1	59.0	55.6	0.93
₩307	51.0	55.5	55.5	1	57.4	55.3	59.0	1.06	53.2	54.8	51.0	0.92
₩401	53.2	57.0	56.6	/	54.0	56.3	63.0	1.11	57.0	58.2	55.5	0.93

slag cement directly from steel slag. It was in 1979 that we shifted to producing SZ cement of (GB) Grade 400. The quality of the SZ cement is satisfactory and stable. It is characterised by the its high wearabity, good corrosion resistance and low hydration heat, therefore especially suitable for engineering projects involving tremendous quantity of concrete pouring, such as underwater engineering, highway and public square construction.

Another advantage which can not be neglected is the production of SZ cement costs much less energy resources than that of ordigary cements of the same grade.

At present in China, the coal consumption for producing slag portland cement of Grade 400 is 116 g/ton, whereas that for producing SZ cement is only 45-50 Kg/ton and the electric power consumption is less, too. Consequently it is economically worthwile to produce the SZ cement. A number of small-scale factories for producing SZ cement are been building in our country.



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