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Short communication

Leaching characteristics of steel slag components and their application in cementitious property prediction

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ABSTRACT

High-efficiency recovery and utilization of steel slag are important concerns for environmental protection and sustainable development. To establish a rapid method to evaluate the cementitious properties of steel slag, leaching tests were carried out on steel slag components via an evaporation–condensation method; the leaching characteristics and mechanism of the slag were also investigated. The relationship between leaching characteristics and cementitious properties, which were represented by mortar compressive strength, was analyzed. Results show that there exist significant differences among the amounts of chemically active leached components. The leaching process can be described by the shrinking unreacted core model controlled by intra-particle diffusion, and is in accordance with Kondo R hydration kinetics equation. The leaching process showed a good linear relationship between the amounts of components leached from steel slag and the mortar compressive strength of cementitious materials prepared from reference cement and steel slag with mass ratios of 50:50 and 70:30. The compressive strengths of mortars subjected to 7, 28, and 90 days of curing can be accurately predicted by the sum of leached ($CaO + Al_2O_3$) obtained after a certain length of leaching time.

1. Introduction

Steel slag, a mass industrial by-product and waste, can be used as a supplementary cementitious material with high properties in cement and concrete [1–5]. However, the cementitious properties of steel slag obtained from different sources significantly vary due to differences in raw material sources, steelmaking processes, and chemical compositions [6–11]. Present evaluations of cementitious properties of steel slag are generally based on strength ratios [12], correlations of composition parameter [13], accelerated chemical methods [14], volume expansion tests [15], and microscopic analyses [8,16]. However, such methods yield poor accuracy or require lengthy testing periods to complete, rendering them impractical for wide-scale use. Thus, a rapid and highly accurate method for evaluating the cementitious properties of steel slag must be developed.

The cementitious properties of steel slag are strongly related to the leaching characteristics of its chemically active components; these components could be used to characterize the cementitious properties of steel slag. In this paper, the leaching characteristics of various chemically active components (CaO, Al_2O_3, and SiO_2) from six kinds of steel slag are analyzed by an evaporation–condensation method that utilizes a new leaching test apparatus with Soxhelt extraction. The aim of this paper is to determine the relationship between the chemical leaching characteristics and cementitious properties of steel slag, and establish the relation model, which could lay the experimental foundation for future steel slag cementitious property predictions.

2. Raw materials and experimental methods

2.1. Materials

Six kinds of steel slag, named 1# to 6#, respectively, were collected from different sources in China, and used in this study. The slags came from Shaogang Iron and Steel Group Co. Ltd., Baosteel Group Corp., Jigang Group Co. Ltd., Handan Iron and Steel Group Co. Ltd., and Guangxi Liuzhou Iron and Steel (Group) Co. Reference cement with 42.5 grade produced by Xingfa Cement Co. Ltd. in Beijing was also used in this study. The chemical compositions and densities of the reference cement and steel slag powders are listed in Table 1.

2.2. Experimental methods

2.2.1. Evaporation–condensation leaching test

Leaching tests were performed on the experimental apparatus, as shown in Fig. 1. The bottom of the apparatus held a flask, which was filled with 300 ml secondary distilled water as a leachant. The

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Table 1
Chemical composition and physical properties of materials.

Sample	Source (City and province of China)	Chemical composition (*w*/%)								Density ($kg\,m^{-3}$)	Specific surface area ($m^2\,kg^{-1}$)
		CaO	SiO_2	Al_2O_3	Fe_2O_3	MgO	SO_3	MnO	f-CaO		
1#	Shaoguan, Guangdong province	40.01	18.94	2.91	8.85	5.36	0.35	2.79	2.79	3300	498
2#	Shaoguan, Guangdong province	49.11	18.18	1.05	7.48	6.74	0.48	2.79	4.34	3270	490
3#	Shanghai	41.06	11.51	1.57	12.29	8.09	0.08	0.42	2.61	3610	496
4#	Handan, Hebei province	44.53	14.84	3.19	9.31	7.50	0.36	0.17	0.73	3430	506
5#	Jinan, Shandong province	45.11	14.99	5.06	14.18	6.69	0.40	1.68	2.88	3390	494
6#	Liuzhou, Guangxi province	38.90	17.12	4.58	8.24	6.99	0.38	2.10	3.43	3240	507
Reference Cement	Beijing	63.11	23.52	4.48	3.04	1.28	2.87	–	0.36	3140	335

top of the flask was connected to an extractor. 3.0000 g of a steel slag powder sample was wrapped with quantitative filter paper and laid at the bottom of this flask. A condenser was fixed on top of the extractor. When the water had been heated to boiling point, the vapor rising through the branch pipe was condensed and allowed to drop into the extractor, where steel slag components can be leached out. Once the leachate level reached the highest position of the siphon, the leachate refluxed back into the flask due to the siphon effect. As the leaching process cycled, different leached chemical steel slag components were concentrated and rapidly separated from the steel slag sample.

2.2.2. *Chemical analysis method*

Three leached chemical components, CaO, Al_2O_3, and SiO_2, were analyzed. Cumulative leached amounts of CaO and Al_2O_3 were determined by EDTA complexometry, while cumulative amounts of SiO_2 were determined by potassium fluorosilicate volumetric analysis.

2.2.3. *Microscopic morphology analysis*

The microstructures of the steel slag samples were analyzed by an XL-30 scanning electron microscope (Philips, Netherlands) with a resolution of 0.35 nm and an accelerating voltage of 0–30 kV.

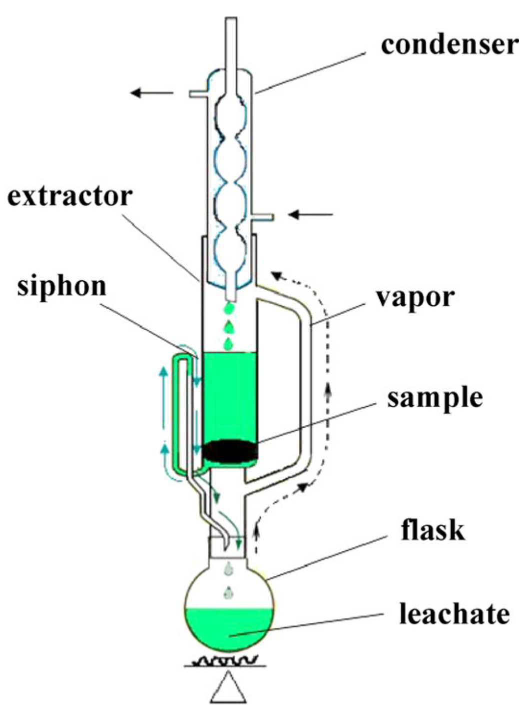

Fig. 1. Leaching test apparatus.

2.2.4. *Preparation of mortars*

Cement mortar prisms of 40 mm × 40 mm × 160 mm were prepared for strength measurements according to Chinese National Standard GB/T 17671-1999 Method of Testing Cements: Determination of Strength. The ratio of cement to steel slag was 50:50 in cementitious system I and 70:30 in cementitious system II; these were prepared according to Chinese National Standard GB/T 18046-2008 Ground Granulated Blast Furnace Slag Used for Cement and Concrete and GB/T 20491-2006 Steel Slag Powder Used for Cement and Concrete, respectively. After demoulding, the specimens were cured in water at 20 ± 2 °C. Strength measurements were carried out after 3, 7, 28, and 90 d of curing.

3. Results and discussion

3.1. *Evaporation–condensation leaching test*

3.1.1. *Amount of leached chemically active components and leaching rate*

The results of the leaching tests are shown in Figs. 2–4. The cumulative leached amounts of all three chemical components investigated increased with leaching time. The largest amount of leached material was CaO, while the smallest was Al_2O_3; these results are in accordance with the chemical compositions of these materials. The leaching rates varied among the components investigated. The leaching rate of Al_2O_3 decreased with leaching time, whereas that of CaO and SiO_2 remained relatively stable. The differences in these leaching characteristics may be used to reflect differences in the cementitious properties of steel slag.

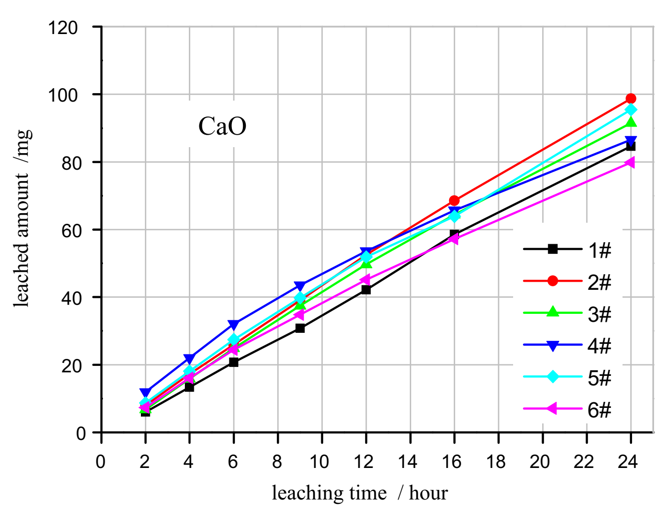

Fig. 2. Amount of leached CaO obtained with different leaching times.

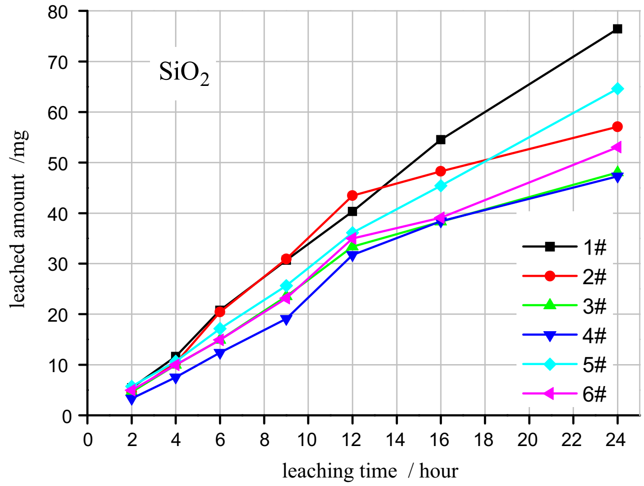

Fig. 3. Amount of leached SiO_2 obtained with different leaching times.

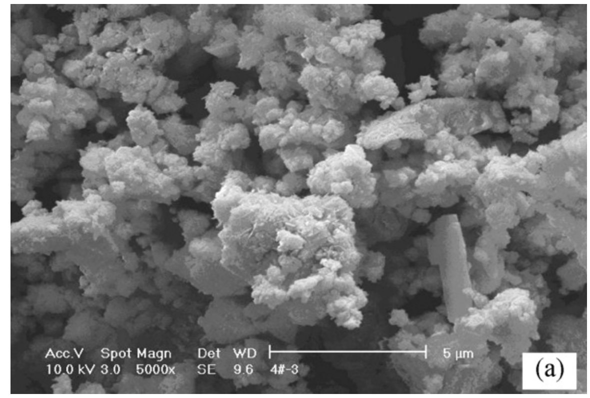

Fig. 5. Morphological characteristics of 4# steel slag before leaching.

3.1.2. Leaching model

The leaching of steel slag components, a liquid–solid uncatalyzed reaction, is actually a hydration reaction. Generally, a liquid–solid uncatalyzed reaction can be described by several models, including the shrinking unreacted core model, the volume reaction model, and the finite reaction model, among others [17,18].

During evaporation–condensation leaching, chemical components leach from the steel slag and react with water. A solid layer forms when part of the insoluble reaction product deposits on the surface of the particle. With continuous leaching, inner steel slag components diffuse through the insoluble solid layer, and the leaching interface shrinks towards the core of the particle. This leaching characteristic can be verified by microstructural analysis, usually by SEM. Taking the 4# steel slag as an example, the particle surface morphology of the slag changed from smooth to cellular and porous (Figs. 5 and 6) after 24 h of leaching, indicating that leaching here occurs in accordance with the characteristics of the shrinking unreacted core model.

3.1.3. Determination of the controlling step

The leaching process described by the shrinking unreacted core model consists of liquid phase diffusion, surface reaction, and internal diffusion, and its development depends on the slowest step [19]. As previously mentioned, chemical components leached from steel slag samples are periodically siphoned and flowed back into the flask. The samples can then be leached by high purity condensed water. Therefore, neither liquid phase diffusion nor surface reaction has significant effects on the leaching process. The controlling step must therefore be internal diffusion.

To confirm the controlling step, α is defined as the leach ratio, which is the ratio of the leached amount of a component to its total mass in the original sample. Calculating the leach ratios at different leaching times according to the results shown in Figs. 2–4, the relationship between the leach ratio and leaching time was found to fit the Kondo R hydration kinetics equation [20], which is expressed as:

$$[1-(1-\alpha)^{1/3}]^N = Kt \quad (1)$$

where α is the leach ratio; t is the leaching time; K is the reaction rate constant; and N is a constant related to the reaction mechanism. When the value of N is above 2, about 1, or below 1, the controlling step of the reaction is internal diffusion, surface reaction, or liquid phase diffusion, respectively [21].

The values of N and K in Formula (1) are calculated according to the slope and intercept of the fitted linear line between $\ln[1-(1-\alpha)^{1/3}]$ and $\ln t$. Fitting results and coefficients of determination are listed in Table 2.

From Table 2, it can be seen that all values of N are far higher than 2. The results confirm the validity of the presumption that the leaching rates of chemically active components are determined by diffusion rates.

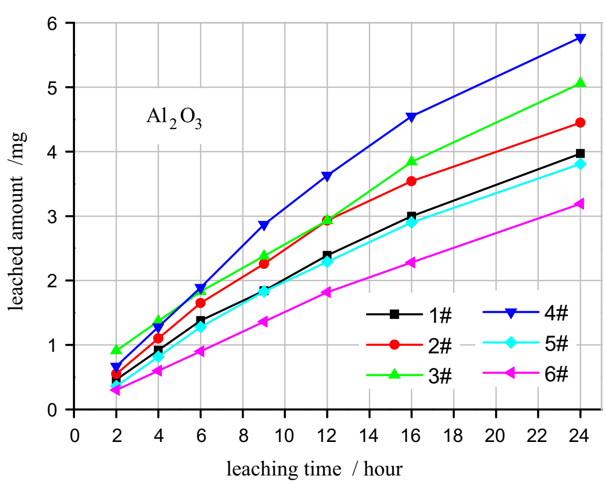

Fig. 4. Amount of leached Al_2O_3 obtained with different leaching times.

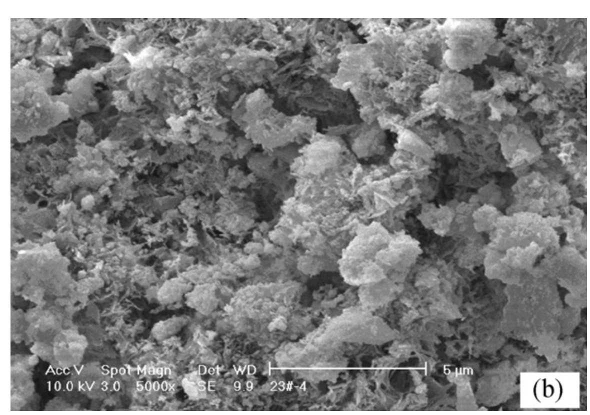

Fig. 6. Morphological characteristics of 4# steel slag after 24 h of leaching.

Table 2
Leaching kinetic parameters of chemically active components.

Sample	CaO			SiO_2			Al_2O_3		
	N	K	R^2	N	K	R^2	N	K	R^2
1#	84.82	5.16×10^{-16}	0.902	48.92	1.18×10^{-09}	0.964	41.08	3.29×10^{-08}	0.963
2#	80.13	3.27×10^{-15}	0.885	41.88	1.83×10^{-08}	0.913	126.90	2.39×10^{-23}	0.941
3#	71.17	1.30×10^{-13}	0.903	39.23	6.11×10^{-08}	0.953	59.52	2.11×10^{-11}	0.912
4#	91.83	3.95×10^{-17}	0.951	48.80	1.10×10^{-09}	0.923	92.94	2.24×10^{-17}	0.948
5#	82.78	1.25×10^{-15}	0.908	39.95	4.15×10^{-08}	0.908	221.24	5.50×10^{-40}	0.950
6#	83.75	8.61×10^{-16}	0.927	53.62	1.70×10^{-10}	0.930	242.13	1.07×10^{-43}	0.917

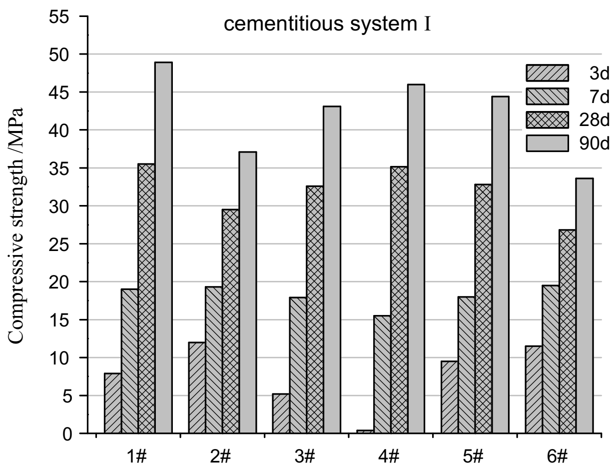

Fig. 7. Mortar compressive strength of cementitious system I.

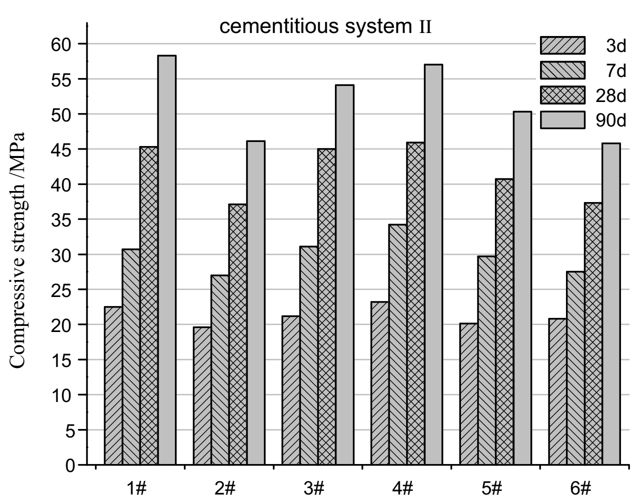

Fig. 8. Mortar compressive strength of cementitious system II.

3.2. Mechanical strength of mortars

The compressive strengths of mortars prepared from steel slag from different sources and reference cement were measured after 3, 7, 28, and 90 d of curing, the results of which are shown in Figs. 7 and 8.

It can be observed that the type of cementitious system strongly influences the compressive strength of the mortar produced. For the same cementitious system, the compressive strengths of mortars prepared from different steel slag sources vary considerably with curing age. These differences reflect complicated actions among bonding components in cementitious materials.

3.3. Prediction of steel slag cementitious properties by their leaching characteristics

A linear correlation coefficient analysis was performed between the cementitious properties of materials from steel slag and the leaching characteristics of the steel slag. The prediction parameters of leaching characteristics include single and complex amounts of leached chemical components at different leaching times and their mutual mole ratios. Cementitious properties were evaluated by the compressive strengths of mortars obtained from steel slag at different curing ages. The correlation coefficients between the cementitious properties and the leaching characteristics were calculated; the results from such calculations yielded a good linear correlation according to the critical value of the correlation coefficient, and are listed in Table 3.

From Table 3, it can be seen that significant correlations, represented by the calculated values of the correlation coefficient r, are higher than the critical value r_α at a certain significance level α. This can be observed between the leaching parameters and compressive strengths of cementitious mortars from steel slag at some curing age. The compressive strengths of mortars cured for 7, 28, and 90 d show the highest degree of linear correlation with the amounts of leached ($CaO + Al_2O_3$) obtained from leaching times of 6, 16, and 16 h, respectively, in cementitious system I, and 9, 16, and 16 h, respectively, in cementitious system II. Therefore, the parameters of leaching characteristics previously mentioned can generally or partially reflect differences in the cementitious properties of steel slag from different sources.

According to the results obtained from the correlation analysis, the mortar compressive strengths of cementitious materials from steel slag can be predicted from their leaching parameters through the following equation:

$$\sigma_c = a + bX \pm uS_y \quad (2)$$

where σ_c is the mortar compressive strength of a cementitious material obtained from steel slag at some curing age (MPa); X is the leached amount (mg); a is a constant term; b is the regression coefficient; S_y is the residual standard deviation (MPa); u is the location parameter of standard normal distribution; $u = 1.96$ for 95% fiducial probability; and $u = 1.65$ for 90% fiducial probability.

The reliability of the prediction equation was tested by the following Chinese National Standards:

- JC 738-2004 Accelerated Test Method for Cement Strength, specifying the coefficient of variability (CV), $CV = S_y/\sigma_{average}$, must be less than 7%
- GB 17671-1999 Method of Testing Cements: Determination of Strength, specifying that the mortar sample with a measured compressive strength beyond ±10% of the average must be abandoned.

In this study, $u\cdot CV \le 10\%$ was adopted in the accuracy test.

Table 3
Results of correlation analysis and prediction of compressive strength.

Cementitious system	X (mg)	Leaching time	Curing age	r	a	b	CV	u·CV	
								u = 1.96	u = 1.65
I	($CaO + Al_2O_3$)	6-h	7-day	−0.897[a]	23.71	−0.63	3.78%	7.40%	6.30%
		16-h	28-day	0.983	−12.12	0.67	2.14%	4.20%	3.60%
		16-h	90-day	0.983	−33.61	1.14	2.76%	5.40%	4.60%
	SiO_2	4-h	7-day	0.842	9.05	0.91	4.90%	9.60%	8.10%
	Al_2O_3	9-h	7-day	−0.829	23.07	−2.33	5.05%	9.90%	8.40%
II	($CaO + Al_2O_3$)	9-h	7-day	0.938	9.52	0.52	3.42%	6.70%	5.60%
		16-h	28-day	0.945	−9.71	0.78	3.57%	7.00%	5.90%
		16-h	90-day	0.975	−18.56	1.06	2.60%	5.10%	4.30%
	SiO_2	2-h	3-day	−0.912	28.40	−1.50	3.01%	5.90%	4.90%
		4-h	7-day	−0.844	46.33	−1.63	5.10%	10.00%	8.70%
	Al_2O_3	9-h	7-day	0.919	20.42	4.60	3.88%	7.60%	6.40%
		9-h	28-day	0.884	27.59	6.84	5.05%	9.90%	8.40%

[a] $r_{0.05} = 0.811$ for 95% probability of a correlation, $r_{0.01} = 0.917$ for 99% probability of a correlation.

Predictions of the cementitious properties of materials obtained from steel slag and the results of the accuracy test are listed in Table 3.

From Table 3, the mortar compressive strengths of cementitious materials from steel slag can be accurately predicted by the corresponding parameters of leaching characteristics with a prediction accuracy of CV < 7% and $u \cdot CV \leq 10\%$. In accordance with the results of the correlation analysis, the most accurate compressive strengths of mortars subjected to 7, 28, and 90 d curing, both in cementitious systems I and II, can be determined from the amount of ($CaO + Al_2O_3$) obtained after a certain length of leaching time. The amount of leached SiO_2 is suitable for predicting the early compressive strengths of the mortars, especially after 3 d of curing, in cementitious system II.

Further studies are necessary to increase the accuracy of predictions. One such study may, for example, include the cement and steel slag as a whole in the evaporation–condensation leaching tests.

4. Conclusion

Evaporation–condensation leaching tests showed that the material with the largest amount of leached chemically active components is CaO; the second is SiO_2, and the last is Al_2O_3. The leaching process can be described by the shrinking unreacted core model controlled by intra-particle diffusion. The relationship between the leaching ratio and the leaching time fits the Kondo R hydration kinetics equation. Parameters of leaching characteristics for different sources of steel slag can reflect differences in their cementitious properties; thus, these characteristics may be used to predict these properties. The compressive strengths of mortars cured for 7, 28, and 90 d can be accurately predicted by the amount of ($CaO + Al_2O_3$) obtained after a certain length of leaching time. Evaporation–condensation leaching tests can therefore be developed into a method for the rapid evaluation of the cementitious properties of steel slag.

Acknowledgments

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