

温度对煤矸石还原钢渣铁氧化物制备的水淬渣活性的影响

宋 强¹, 聂 娇¹, 宋甜甜¹, 胡亚茹¹, 邓 洋², 陈延信¹, 程福安¹

(1. 西安建筑科技大学材料科学与工程学院, 西安 710055; 2. 陕西富平生态水泥有限公司, 陕西 渭南 711709)

摘 要: 钢渣中的铁氧化物是影响钢渣粉活性的因素之一。为改善钢渣粉水化活性, 实现钢渣和煤矸石协同处置, 利用煤矸石中残碳还原和分离出钢渣中的铁, 研究了不同温度下煤矸石与钢渣制备的水淬残渣的物相变化以及水化活性。结果表明: 提高还原温度, 可以显著提高铁的回收率, 最高可达 94%。还原温度低于 1 450 °C 时, 水淬残渣中的矿物相主要为钙镁蔷薇辉石和钙铝黄长石。随着温度分别升高到 1 450 °C 和 1 500 °C, 钙镁蔷薇辉石和钙铝黄长石相消失。此时, 水淬残渣主要由玻璃相组成。还原温度升高导致水淬残渣中玻璃相含量增多, 胶凝活性增强, 掺加高还原温度水淬渣的水泥水化反应累计放热量更大。

关键词: 钢渣; 煤矸石; 碳热还原; 水淬残渣; 水化活性

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钢渣中铁氧化物含量在 14%到 29%之间^[1], 一般以 RO 相(CaO-FeO-MnO-MgO 固溶体)、FeO_x、C₂F 等矿物相存在, 这些矿物相对钢渣粉水化活性几乎没有贡献^[2-4]。一些研究使用 H₂、CO、无烟煤、碳化硅、碳粉等还原剂将钢渣中的铁氧化物熔融还原成铁合金, 得到的水淬残渣用作辅助胶凝材料, 从而实现钢渣分质利用的目的^[5-10]。

从还原效果和经济性上来看, 碳热还原是较为适宜的方法。Lindval 等^[6]以无烟煤和碳化硅为还原剂, 获得富含 Fe、Mn、V 和 Cr 的金属, 并初步探索了将残渣用作辅助胶凝材料的可行性, 但未对铁的回收效率和残渣性质进行阐述。Liu^[7]在钢渣中添加 7%的碳粉和 SiO₂、Al₂O₃ 等组分调节材料, 以提高玻璃相、C₂S 和 C₃S 的含量。给出的 C₃S 形成和减少 f-CaO 的最佳 CaO/(SiO₂+Al₂O₃) 比为 1.98~2.59。Guo 等^[8]利用高岭土和碳对钢渣进行改质和还原, 当 (CaO+MgO)/(SiO₂+Al₂O₃) 比在 0.97~1.31 时, 铁的回收率达到 95%以上。掺 30%残渣的水泥 28 d 最高强度为 55.1 MPa。Lee 等^[9]用焦炭还原钢渣, 在微波条件下铁的回收率最高达 87%, 渣和金属分离效果

明显, 还原尾渣可添加至水泥熟料中。殷素红等^[10]使用碳粉、石灰和黏土直接还原和熔融重构了钢渣, 结果表明熔融还原比直接还原更易实现渣铁分离, 水化活性更高。杨曜等^[11]利用煤矸石作为还原材料, 在 1 500 °C 高温熔融还原钢渣回收 Fe, 还原所得铁回收率最高可达 96.0%, 精矿铁品味最高为 86.75%, 残渣矿物相主要为 Ca₃MgSi₂O₈ 和 CS, 28 d 最高抗压强度为 46.5 MPa, 但并未探讨还原温度对钢渣还原效率和残渣胶凝活性的影响。郭辉^[12]利用煤矸石作为还原剂, 在 1 500 °C 研究不同掺量对钢渣铁还原的影响, 单质铁回收率最高可达 95.3%, 但并未对回收所得精矿铁品位进行阐述, 残渣主要矿物相为 Ca₃MgSi₂O₈ 和 C₂S, 28 d 最高抗压强度为 52.3 MPa。

钢渣还原过程为 FeO_x 和 C₂F 被固体 C 还原, FeO_x 的还原顺序是由高价氧化物依次向低价氧化物反应的, 即 Fe₂O₃→Fe₃O₄→FeO→Fe, 简化的反应方程式见式(1)。



为提高固体废弃物的利用率, 达到以废制废的目的, 本工作以煤矸石的残碳作为还原剂, 研究了不

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第一作者: 宋 强(1980—), 男, 博士, 副教授。

通信作者: 陈延信(1974—), 男, 博士, 教授;

程福安(1965—), 男, 硕士, 教授。

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First author: SONG Qiang (1980—), male, Ph.D., Associate Professor.

E-mail: sqxauat@126.com

Correspondent author: CHEN Yanxin (1974—), Ph.D., Professor.

CHENG Fuan (1965—), Master, Professor.

E-mail: yx_ch@126.com; Chengfuan@xauat.edu.cn

同温度下钢渣中铁的回收率以及水淬残渣水化特点。

1 实验

1.1 材料

水泥是混凝土外加剂检验专用基准水泥。钢渣是陕西龙门钢铁(集团)有限责任公司的转炉钢渣。煤矸石来自安徽海螺集团有限责任公司。水泥、钢渣和煤矸石化学成分见表 1, X 射线衍射谱(XRD)

见图 1~图 2。

钢渣中的矿物相包括 C_2S 、 Fe_2O_3 、 FeO 、 Fe 、方镁石、RO 相 $[(MgO)_{0.239}(FeO)_{0.761}]^{[13]}$ 、白硅钙石 $[Ca_{14}Mg_2(SiO_4)_8]$ 和黑钙铁石 $(Ca_2Fe_2O_5)$ 。煤矸石主要矿物相有埃洛石 $[Al_2Si_2O_5(OH)_4 \cdot 2H_2O]$ 、石英(SiO_2)、方解石($CaCO_3$)和高岭石 $[Al_2(Si_2O_5)(OH)_4]$ 。

依照 GB/T 212—2008《煤的工业分析方法》测定煤矸石工业分析数据见表 2。

表 1 原料的化学组成
Table 1 Chemical composition of raw materials

Material	CaO	Fe ₂ O ₃	SiO ₂	MgO	Al ₂ O ₃	MnO	P ₂ O ₅	TiO ₂	SO ₃	Na ₂ O
Cement	64.02	3.15	21.14	2.57	4.69				2.09	0.30
Steel slag	37.93	20.33	17.22	9.11	5.14	4.50	2.65	1.32	0.34	0.31
Coal gangue	8.17	6.08	54.64	1.01	22.99	0.09	0.09	1.78	1.54	0.42

w is mass fraction.

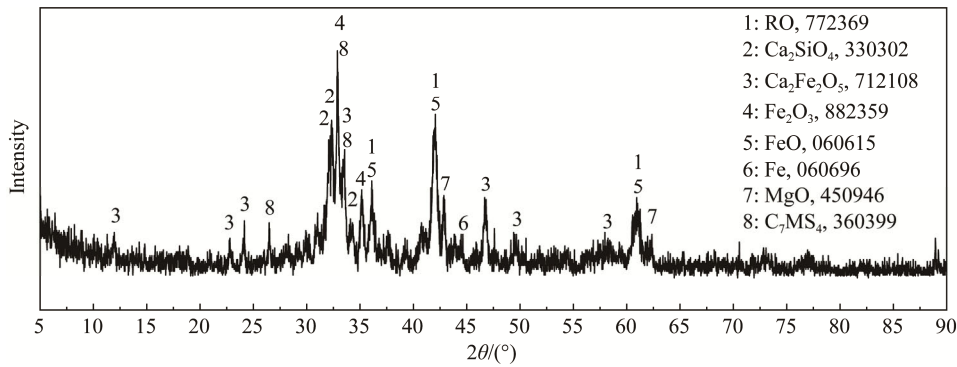


图 1 钢渣的 XRD 谱
Fig. 1 XRD patterns of steel slag

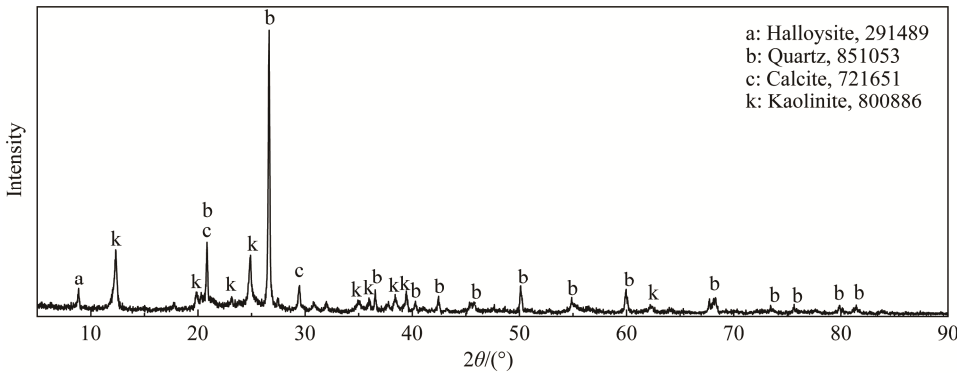


图 2 煤矸石的 XRD 谱
Fig. 2 XRD patterns of coal gangue

表 2 煤矸石的工业分析

Table 2 Industrial analysis of coal gangue				w/%
Water	Ash	Volatile	Fixed carbon	
1.69	60.70	20.77	16.84	

1.2 钢渣还原实验

按照式(1)、表 1 中钢渣和煤矸石 Fe_2O_3 含量以及表 2 中煤矸石的固定碳含量, 计算钢渣和煤矸

石配料比例。为保证还原充分, 在理论煤矸石需要量的基础上增加 10%, 煤矸石占混合料 24.56% (表 3)。

用球磨机粉磨钢渣和煤矸石, 使用 200 目方孔筛筛分得到钢渣粉和煤矸石粉。按照表 3 配料比例将钢渣粉与煤矸石粉混合均匀。混合物料的化学组成如表 4 所示。混合料放入刚玉坩埚并在微波马弗

炉(MOBILELAB-M, 唐山纳源微波热工仪器制造有限公司)中加热还原。在氩气保护气氛中(3 L/min),以 40 ℃/min 的加热速率将混合料分别升温至 1 200、1 300、1 350、1 400、1 450 ℃和 1 500 ℃,保温 30 min 后立即将坩埚取出,放入水

盆中水淬。水淬渣经过烘干,剥离出铁粒,剩余物使用振动磨(ZHM-1A, 北京众合创业科技发展有限公司,设置粉磨时间 1 s)粉磨后磁选出富铁颗粒,其他剩余物称为水淬残渣。水淬残渣化学成分见表 5。

表 3 钢渣和煤矸石中混合料配比
Table 3 Proportion of mixture of steel slag and coalgangue

m/g			Mass fraction of coal gangue in the mixture/%
Steel slag	Theoretical demand for coal gangue	Actual amount of coal gangue added	
100.00	29.60	32.56	24.56

表 4 混合料化学组成
Table 4 Chemical composition of mixture of steel slag and coal gangue

TFe	Fe	FeO	Fe ₂ O ₃	CaO	SiO ₂	MgO	Al ₂ O ₃	MnO	P ₂ O ₅	TiO ₂	SO ₃	Na ₂ O
10.84	0.31	2.67	12.08	30.62	26.41	7.12	9.52	3.42	2.02	1.43	0.63	0.34

TFe is content of all iron elements.

表 5 水淬残渣化学组成
Table 5 Chemical composition of quenched residue

Temperature/℃	Fe ₂ O ₃	CaO	SiO ₂	Al ₂ O ₃	MgO	K ₂ O	Na ₂ O	SO ₃	P ₂ O ₅	MnO	TiO ₂	Other
1 100	13.50	35.87	25.03	9.20	8.23	0.38	0.27	0.43	1.22	3.80	1.43	0.64
1 200	12.54	36.82	24.91	9.04	8.15	0.31	0.25	0.45	1.22	4.07	1.56	0.68
1 300	5.72	40.62	26.69	9.83	8.71	0.32	0.26	0.43	0.89	4.20	1.70	0.63
1 350	1.51	41.87	27.25	10.57	9.12	0.37	0.27	0.41	1.04	5.02	1.80	0.77
1 400	1.74	41.41	27.47	11.41	9.17	0.35	0.27	0.31	0.83	4.71	1.75	0.58
1 450	0.83	41.61	26.46	14.49	8.97	0.30	0.23	0.13	0.43	4.38	1.71	0.46
1 500	0.93	39.18	24.05	19.67	8.07	0.28	0.22	0.07	0.41	4.80	1.66	0.66

1.3 水淬残渣水化实验

在振动磨中将还原处理得到的水淬残渣粉磨(设置粉磨时间 20 s)得到水淬残渣粉(粒度分布见图 3)。在基准水泥中掺入 30%残渣粉,以 0.4 的水灰比制成 40 mm×40 mm×40 mm 净浆试件,在标准

养护箱中养护至 3、7、28 d。使用异丙醇将不同龄期净浆试样中止水化,放入真空干燥箱在 40 ℃温度下烘干至质量不变。掺入不同温度还原的残渣粉的水泥净浆样品命名为:还原温度+J。例如 1 400J,表示掺入 30% 1 400 ℃还原得到的残渣粉的水泥净浆。

水泥胶砂强度按照 GB/T 17671—1999《水泥胶砂强度检验方法(ISO)》标准测试。胶砂样品水灰比为 0.5,胶砂比 1:3,胶凝材料中基准水泥和水淬渣质量比为 7:3,试件尺寸为 40 mm×40 mm×160 mm,试件标准养护到规定龄期测试抗折、抗压强度。

1.4 表征方法

采用日本理学 Rigaku 型 X 射线衍射仪测定矿物相,测试参数为 Cu 靶 K_α 线,管压 40 kV,管流 30 mA,连续扫描方式,扫描速率为 10 (°)/min。采用 Rietveld 定量分析方法对水淬残渣中的玻璃体含量进行计算。用瑞士梅特勒-托利多公司 TGA/DSC1/1600 同步热分析系统进行热重分析(TGA),温度准

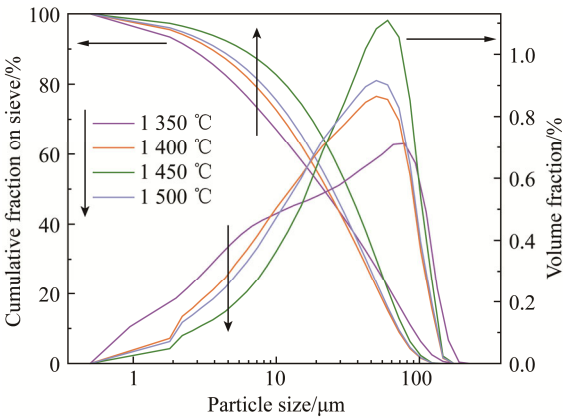


图 3 水淬残渣粉的粒度分布

Fig. 3 Particle size distribution of ground quenched residue

确度: $\pm 0.5^{\circ}\text{C}$ 。采用美国热电公司 Nicolet IS50 Fourier 漫反射红外光谱仪测试红外光谱 (FTIR), 分辨率为 4 cm^{-1} , 扫描累加次数为 32 次, 光栏为 $20\text{ pm}\times 20\text{ pm}$ 。采用德国蔡司 GeminiSEM 500 场发射扫描电镜 (SEM) 观察样品断面形貌, 测试微区元素分布。用 TAM-air (8 通道) 水化量热计分析热释放过程。

2 结果与讨论

2.1 水淬残渣组成

水淬残渣化学成分见表 5。从表 5 可知, $1\ 100^{\circ}\text{C}$ 还原残渣中的 Fe_2O_3 含量从 15.50% (表 4) 下降了 2.00%。随着还原温度升高, Fe_2O_3 含量逐渐降低, 特别是温度超过 $1\ 300^{\circ}\text{C}$, 还原率明显提高, 但是温度超过 $1\ 350^{\circ}\text{C}$ 后, 残渣中的 Fe_2O_3 含量基本保持不变。

图 4 为水淬残渣的 XRD 谱。Rietveld 定量分析谱和水淬残渣玻璃体含量如图 5、图 6 所示。可以看出 $1\ 100^{\circ}\text{C}$ 还原残渣中形成了钙镁蔷薇辉石 ($\text{Ca}_3\text{MgSi}_2\text{O}_8$)、钙铝黄长石 ($2\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{SiO}_2$)^[8]。升高温度钙镁蔷薇辉石含量增加, 钙铝黄长石含量降低。温度升高到 $1\ 350^{\circ}\text{C}$, 钙铝黄长石衍射峰逐渐消失, 同时 2θ 在 32° 左右出现轻微小包峰。还原温度继续升高, 钙镁蔷薇辉石衍射峰高度持续降低, 温度超过 $1\ 450^{\circ}\text{C}$ 后, 该矿物衍射峰基本消失。这是由于在其他条件相同的情况下, 冷却起始温度是影响玻璃化程度的最重要的因素^[14]。温度升高, 晶体衍射峰面积逐渐减小, 还原温度超过 $1\ 450^{\circ}\text{C}$ 后, 水淬残渣主要是玻璃体。Rietveld 定量分析 R_{WP} 介于 10.68%~12.41%, 均小于 15%, 说明拟合数据较为

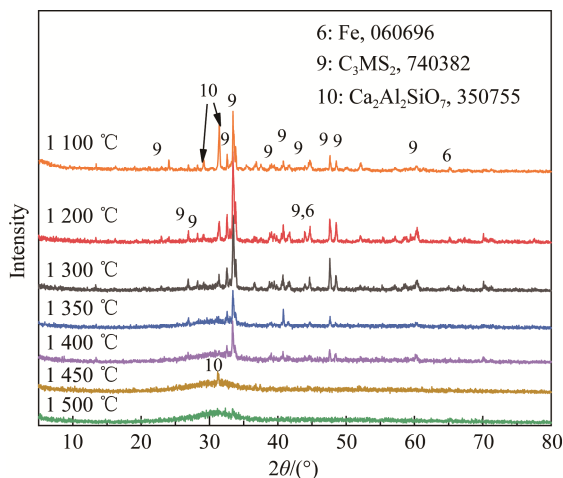


图 4 不同温度水淬残渣 XRD 谱

Fig. 4 XRD patterns of residue slag reduced at different temperatures

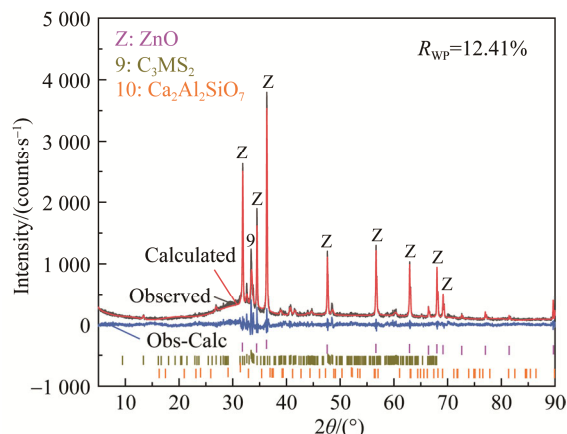


图 5 Rietveld 定量分析的 $1\ 400^{\circ}\text{C}$ 水淬渣 XRD 谱

Fig. 5 Refined XRD patterns of residue slag reduced at $1\ 400^{\circ}\text{C}$ based on Rietveld quantitative analysis

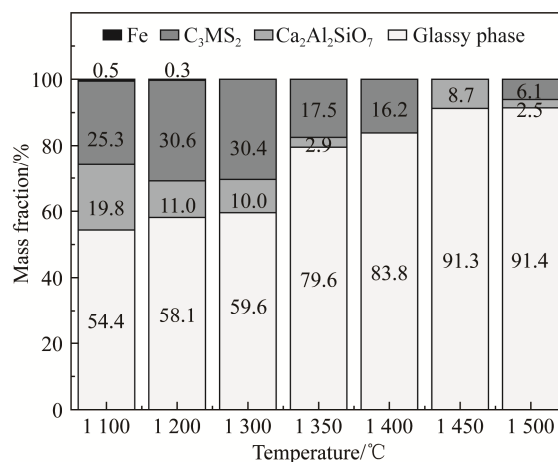


图 6 不同温度水淬残渣物相含量

Fig. 6 Phase content of residue slag reduced at different temperature

合理。还原温度 $1\ 300^{\circ}\text{C}$ 以下, 残渣中的玻璃体含量小于 60%, 温度达到 $1\ 350^{\circ}\text{C}$, 玻璃体含量增加迅速, 接近 80%, 继续升高还原温度到 $1\ 450^{\circ}\text{C}$, 玻璃体含量超过 90%。

图 7 是 $1\ 400^{\circ}\text{C}$ 还原所得水淬残渣 SEM-EDS 图。图 7a 中 1、2、3 点和图 7b 中 6 点是呈条状、树枝状的钙镁蔷薇辉石。图 7b 中 4 点和 5 点为单质铁, 水淬残渣中依然含有部分未完全分离的金属铁。

不同温度还原的残渣红外光谱如图 8 所示。 434 cm^{-1} 处的谱带是由于 Si—O 键振动^[15], 410 、 467 cm^{-1} 为 AlO_6 —O 八面体基团的吸收峰^[16], 505 cm^{-1} 为 AlO_6 八面体的吸收峰^[17], 随着还原温度升高, 吸收峰逐渐消失。

波数 484 cm^{-1} ^[18-19] 和 535 cm^{-1} ^[18, 20-21] 的吸收峰属于黄铁矿。 587 cm^{-1} 的吸收峰属于磁铁矿^[19-21]。随着还原温度升高, 3 个吸收峰强度逐渐降低, 说明还原温度越高, 铁氧化物还原率越高。

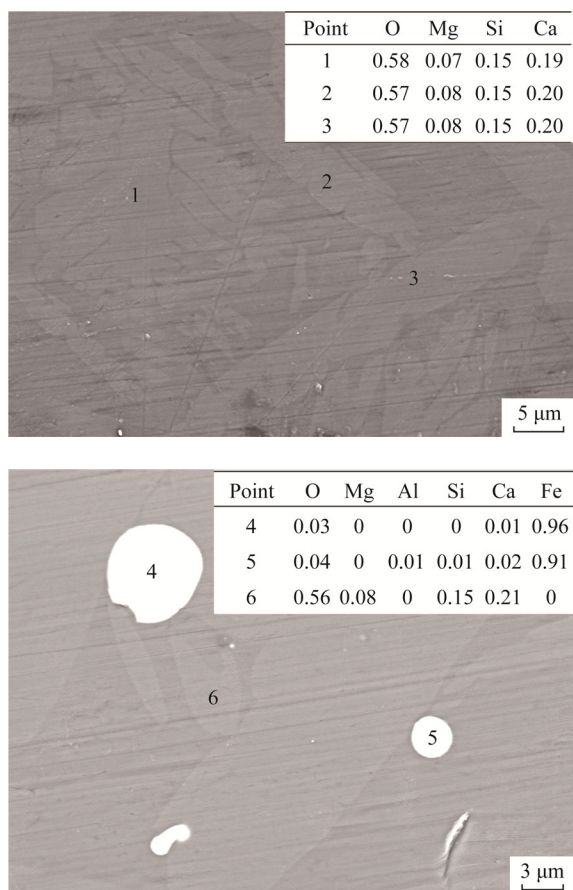


图7 1400 °C还原的残渣 SEM 照片和 EDS 数据

Fig. 7 SEM images and EDS data of residue slag reduced at 1400 °C

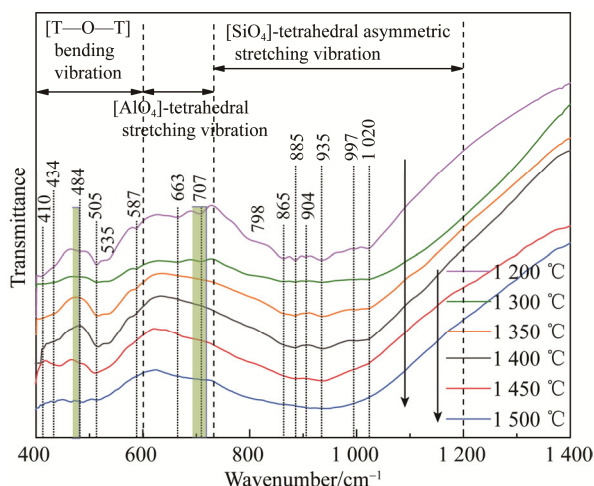


图8 水淬残渣红外光谱

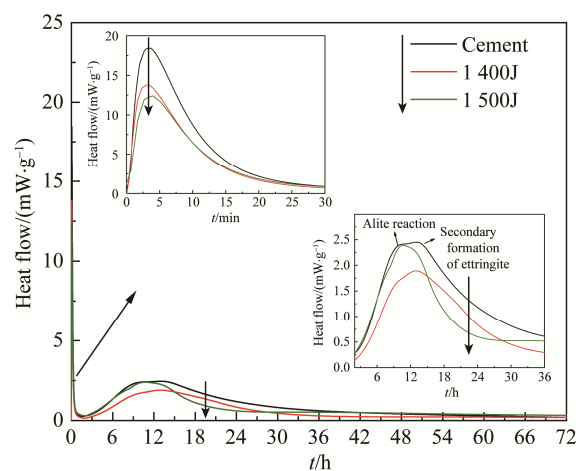
Fig. 8 FTIR spectra of residue slag reduced

波数 865, 885, 904, 935, 997 cm^{-1} 和 1020 cm^{-1} 的 6 个吸收带归属钙镁蔷薇辉石^[22], 这些吸收带是 Si—O 对称和非对称伸缩振动造成的^[23]。随着还原温度升高这些吸收带强度减弱, 1500 °C 时, 钙镁蔷薇辉石谱带全部消失。

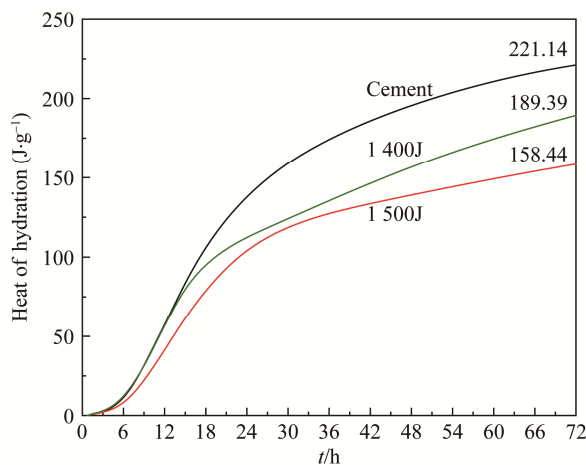
碱性玻璃红外光谱上, 波数 800~1200 cm^{-1} 被分配给 $[\text{SiO}_4]$ 非对称伸缩振动, 600~800 cm^{-1} 则属于 $[\text{AlO}_4]$ 四面体伸缩振动, 400~630 cm^{-1} 则是 T—O—T 弯曲振动造成的^[23]。其中 690~720 cm^{-1} 是由于 $[\text{FeO}_4]$ 四面体伸缩振动造成的, 460~480 cm^{-1} 是 $[\text{FeO}_6]$ 对称伸缩振动造成的^[24]。随着温度升高, 上述 3 个区域谱线逐渐光滑, 铁氧化物对应的振动带逐渐消失。

2.2 水淬残渣水化

图 9a 和图 9b 分别是基准水泥和掺 30% 水淬残渣水泥的水化放热速率曲线和累积放热曲线。



(a) Heat flow



(b) Total heat

图9 基准水泥和掺 30% 1400、1500 °C 水淬残渣的水泥净浆的水化热曲线

Fig. 9 Heat flow and total heat of the reference cement and cement with 30% 1400, 1500 °C residue slag reduced

从图 9a 可以看出, 掺水淬残渣水泥第 1 放热峰低于基准水泥, 且样品 1400J 高于样品 1500J。该放热峰被认为是水泥粉末润湿、矿物溶解、熟料 C_3A

水化造成的^[14, 25-26], 造成 1 400J 放热峰略高于 1 500J 样品的原因可能是 1 400 °C 还原残渣粉末粒度略细。基准水泥的第 2 放热峰是由 C_3S 水化放热峰和 1 个形成二次钙矾石的放热峰组成^[26]。样品 1 500J 第 2 放热峰和基准水泥放热峰峰高接近, 但二次钙矾石形成放热峰有所降低, 这可能是由于加入水淬残渣后体系的 SO_3^{2-}/Al^{3+} 比减小导致该放热峰出现时间提前^[27], 并与 C_3S 第 2 放热峰合并为 1 个弱肩峰, 也是与 C_3S 的第 2 放热峰峰高接近且峰型变窄的可能原因。1 400J 的第 2 放热峰较 1500 J 的放热峰峰高降低 1 mW/g 左右。较低的放热速率应该是 1 400J 样品中含有结晶相造成的。

从图 9b 可以看出, 随着还原温度升高, 水化放热量增加, 1 400 °C 和 1 500 °C 放热量为基准水泥的 71.65% 和 85.64%。这是由于高还原温度导致高玻璃化程度, 进而提高了水淬残渣的水化活性^[14]。

图 10 和图 11 为掺 30% 水淬残渣的水泥水化 3、28 d 的 XRD 谱。随着还原温度升高和水化时间延长, $Ca(OH)_2(CH)$ 的衍射峰逐渐降低。水淬残渣与水泥水化产物 CH 发生反应, 消耗了 CH, 并且随着钢渣还原温度升高, 残渣火山灰效应提高, 相应的残渣水泥中 CH 量降低。

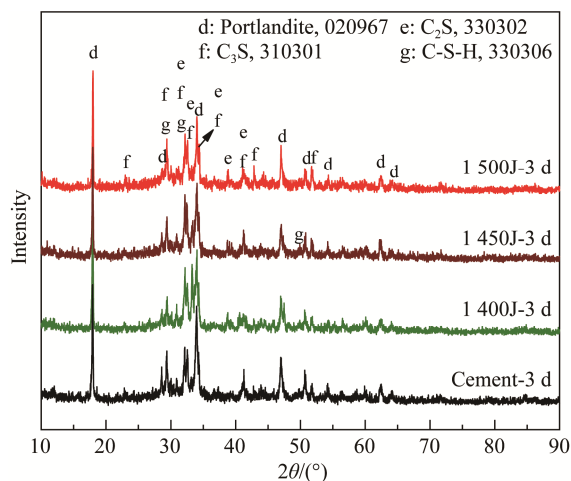
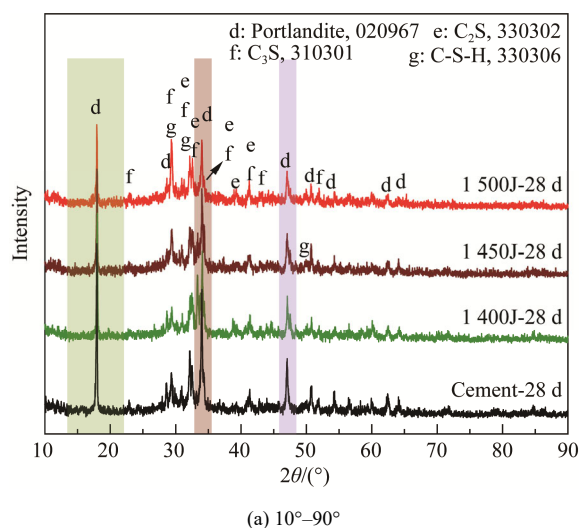


图 10 水化 3 d XRD 谱

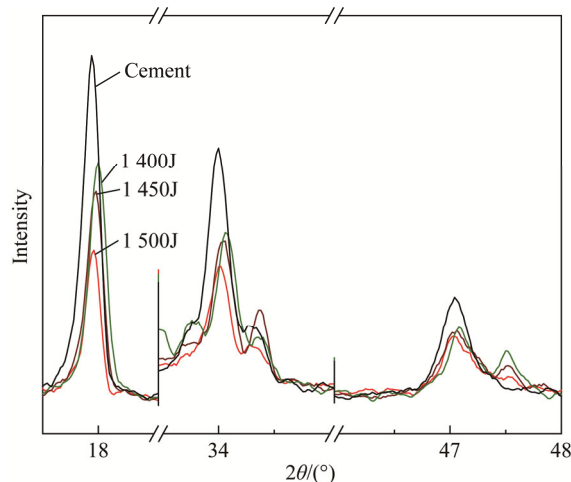
Fig. 10 XRD patterns of the samples after hydration for 3 d

掺加水淬残渣的水泥水化 3 d, 28 d 红外光谱见图 12~图 13。444、515 cm^{-1} 处的吸收带为 Si—O—Si 键的振动^[28-29], 710 cm^{-1} 处的吸收是由 Si—O—Si(Al) 键的振动引起的^[30], 874 cm^{-1} 和 1 420~1 480 cm^{-1} 处的吸收带是属于 O—C—O 伸缩振动^[17, 31]。3 d 和 28 d 水化产物谱带上, 该吸收带随着残渣还原温度增加强度逐渐增强, 说明还原温度更高的残渣水化活性更高, 导致体系中的 CH 含量降低后, 水

泥更易碳化。960~1 040 cm^{-1} 中的强烈振动归因于 Si—O—Si 键的不对称伸缩振动, 归属于 C-S-H



(a) 10°-90°



(b) 17.5°-48.0°

图 11 水化 28 d 样品的 XRD 谱

Fig. 11 XRD patterns of the samples after hydration for 28 d

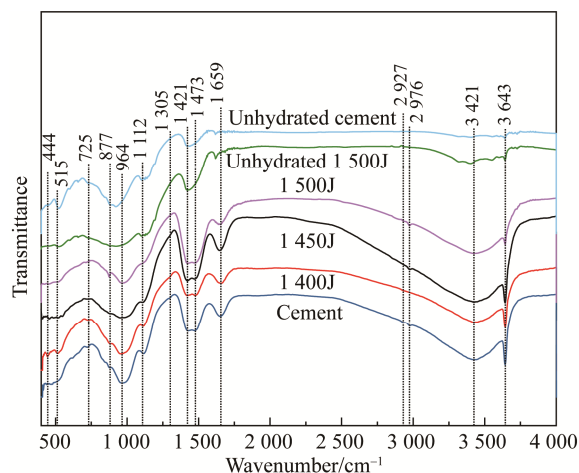


图 12 水化 3 d 样品的 FTIR 谱

Fig. 12 FTIR spectra of the samples after hydration for 3 d

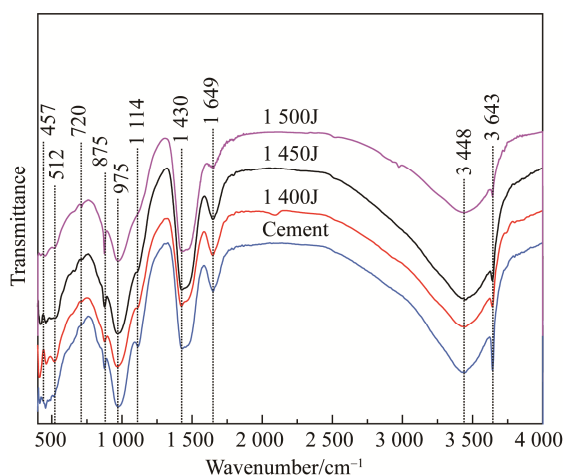


图 13 水化 28 d 样品的 FTIR 谱

Fig. 13 FTIR spectra of the samples after hydration for 28 d

相^[17, 32]。3 d 水化试样谱线上, 1 112、1 114 cm^{-1} 的峰值归属于硫酸盐中 $[\text{SO}_4]$ 的 S—O 键振动^[30], 该吸收带在钙矾石(AFt)的谱带上被观察到^[33], 1 660 cm^{-1} 吸收带是 AFt 的 O—H 振动造成的。1 400J, 1 450J, 1 500J 样品的这 2 个振动带比基准水泥的强度低, 表明形成的 AFt 含量更少。28 d 时, 各个样品中 1 114 cm^{-1} 附近的吸收带有所减弱, 1 660 cm^{-1} 吸收带转变到 1 649 cm^{-1} , 1 650 cm^{-1} 附近的吸收带

是 AFm 的 O—H 振动造成的^[34], 说明 AFt 转变为 AFm。O—H 的伸缩振动峰出现在波数 3 443 cm^{-1} 处^[29], 表明含有结合水或层间水^[17, 35]。

吸收带出现在 3 643 cm^{-1} 归属于 CH 的 OH 基团^[17], 与纯水泥相比, 掺加水淬残渣的样品 CH 的 O—H 键振动减弱, 表明残渣与水泥中的氢氧化钙进行反应, 并且随着还原温度升高, 反应更加剧烈, 随着反应时间延长, 与 3 d 红外光谱相比, 28 d 3 643 cm^{-1} 处的吸收峰强度进一步降低。

图 14 为水泥和掺水淬残渣样品 3、28 d 的热重曲线。按照参考文献[36]将曲线划分为 3 段: 145~350 $^{\circ}\text{C}$ 为 C-S-H 脱水, 记为 w_1 ; 400~500 $^{\circ}\text{C}$ 为 CH 脱水, 记为 w_2 ; 600~800 $^{\circ}\text{C}$ 为 CaCO_3 脱碳^[37], 记为 w_3 。按照式(2), 式(3)分别计算 CH 和 CaCO_3 含量。从图 14 和表 6 可以看出, 水化 3 d 时, 1 450J 样品的 C-S-H 含量略高于样品 1 400J 的, 但二者的 CH 含量基本相当, 同时水泥样品发生轻微碳化。水化 28 d 后, 1 450J 比 1 400J 的 CH 含量略低, CaCO_3 含量更高, 这与 FTIR 数据一致。

$$f_{\text{CH}} = \frac{M_{\text{CH}} \times w_2}{M_{\text{H}_2\text{O}}} = 4.11w_2 \quad (2)$$

$$f_{\text{CaCO}_3} = \frac{M_{\text{CaCO}_3} \times w_3}{M_{\text{CO}_2}} = 2.27w_3 \quad (3)$$

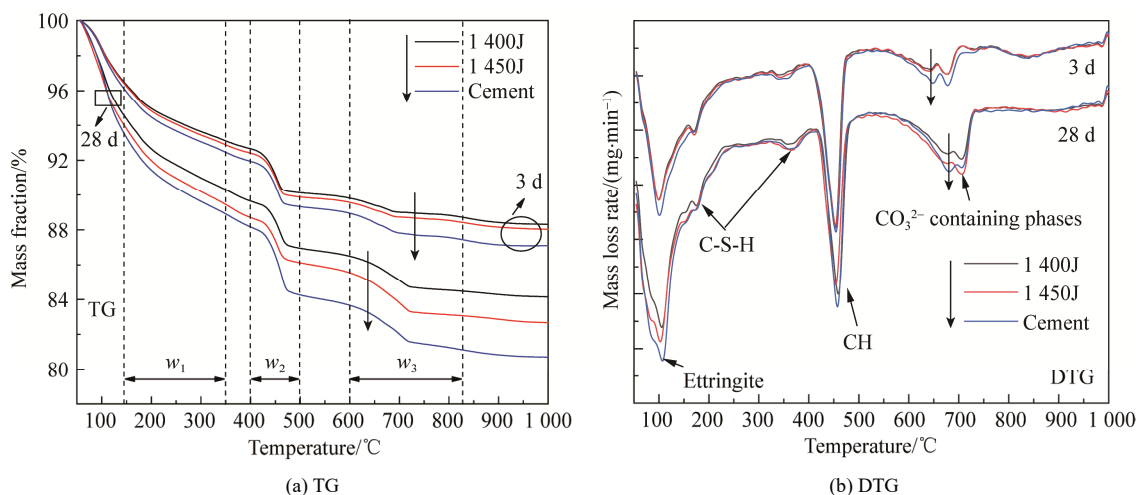


图 14 基准水泥和掺 30% 水淬残渣的水泥水化 3、28 d TG 和 DTG 曲线

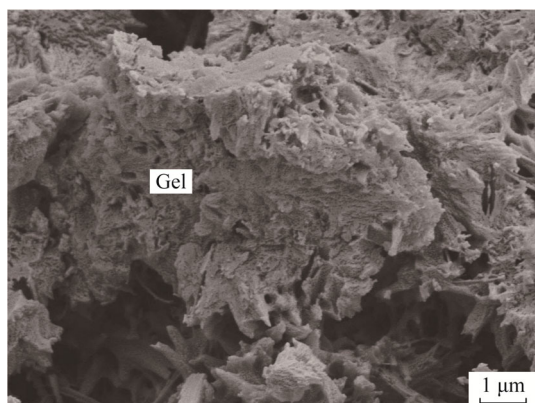
Fig. 14 TG and DTG curves of the reference cement and cement with 30% residue slag after hydration for 3 d and 28 d

表 6 掺水淬残渣的水泥水化 3、28 d 的 CH, CaCO_3 含量以及 C-S-HTable 6 Mass fraction of CH, CaCO_3 and C-S-H in the pastes after 3 d and 28 d hydration

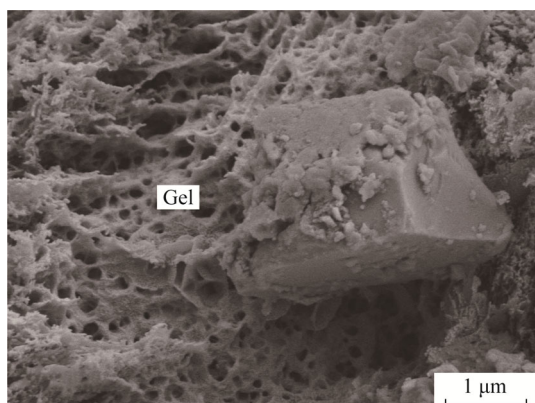
w/%

Samples	3 d					28 d				
	w_1	w_2	w_3	$w(\text{CH})$	$w(\text{CaCO}_3)$	w_1	w_2	w_3	$w(\text{CH})$	$w(\text{CaCO}_3)$
1 400J	3.82	2.53	0.98	10.40	2.22	4.92	2.70	1.96	11.09	4.44
1 450J	4.00	2.53	1.03	10.40	2.34	5.31	2.58	2.42	10.60	5.50
Cement	4.44	3.63	1.77	14.91	4.03	5.37	3.91	2.42	16.08	5.50

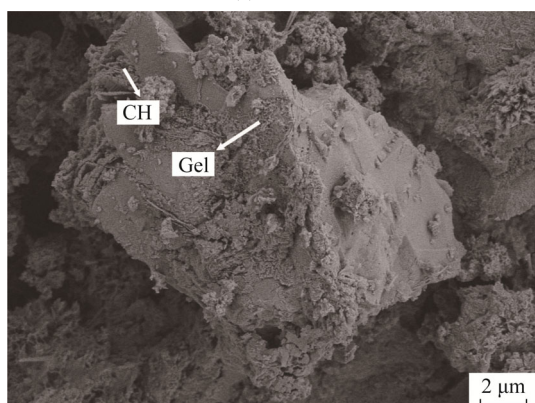
图 15 为掺水淬残渣水泥水化 28 d 的 SEM 照片。由图 15a 可见, 掺 30% 1 500 °C 水淬残渣的样品颗粒表面被 C-S-H 凝胶包裹; 由图 15b 可见, 掺 30% 1 450 °C 水淬残渣的样品颗粒未完全水化, 但是左侧表面已生成网状 C-S-H; 由图 15c 可见, 掺 30% 1 400 °C 水淬残渣的样品颗粒表面有少量水化产物生成。水淬残渣颗粒表面水化产物的形成状态和含量可以反映水淬残渣的胶凝活性, 随着还原温度下降, 水淬残渣胶凝活性逐渐降低。



(a) 1 500J



(b) 1 450J



(c) 1 400J

图 15 掺 30% 1 500、1 450 °C 和 1 400 °C 水淬残渣 28 d 水化产物微观形貌照片

Fig. 15 SEM images of cement with 30% residue slag reduced after 28 d hydration at 1 500, 1 450 °C and 1 400 °C

2.3 水淬残渣水泥胶砂强度

图 16 为掺加 30% 在 1 400, 1 450 °C 和 1 500 °C 还原的水淬残渣的水泥和基准水泥抗折、抗压强度。

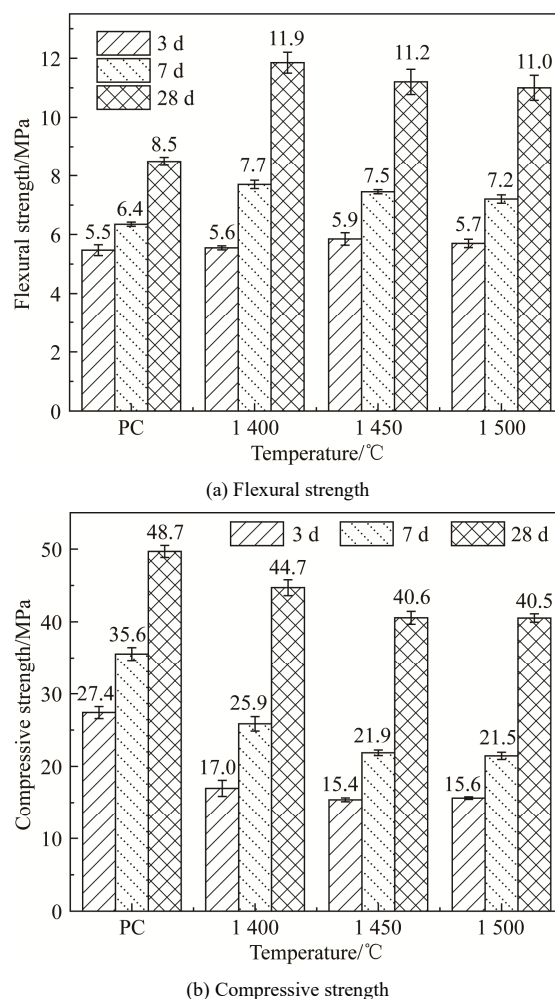


图 16 掺加 30% 水淬残渣水泥砂浆的强度

Fig. 16 Strength development of mortars with 30% residue

由图 16 可见, 掺加 30% 残渣的水泥 3 d 抗折强度与基准水泥基本相当, 养护时间越长, 残渣水泥抗折强度增长速度高于基准水泥, 28 d 强度比基准水泥高出 30%。这得益于残渣消耗 CH, 细化孔结构, 改善浆体和骨料粘结等因素。残渣水泥 3 d 抗压强度约为基准水泥的 60%。残渣水泥水化速率高于基准水泥, 水化 28 d 后, 1 400 °C 制备的残渣水泥强度达到基准水泥强度 90%, 但其他 2 种渣的强度则仅仅为基准水泥的 82%。1 400 °C 还原残渣制备的水泥具有最高的强度, 造成这一结果的原因还需要进一步研究。

3 结论

采用含碳煤矸石还原钢渣中的铁氧化物, 熔融还原得到的熔渣水淬后, 研究了水淬残渣的物相组

成, 以及对水化活性的影响。主要结论包括:

1) 1 300 °C 还原, 钢渣中的 FeO_x 的回收率只有 63%, 升高温度 FeO_x 还原率以及铁品位增加。还原温度高于 1 450 °C 时, 回收率维持在 94% 左右。

2) 还原温度低于 1 300 °C, 水淬残渣的矿物相主要为钙镁蔷薇辉石和钙铝黄长石。随着温度升高, 结晶相逐渐减少, 1 500 °C 时主要是玻璃相。

3) 还原温度升高水淬残渣中玻璃相含量增多, 胶凝活性增强。水泥水化产物中的 CH 与水淬残渣反应, 掺加高还原温度水淬渣的水泥中剩余的 CH 含量更低, 水泥水化反应累计放热量更大, 碳化程度更高。

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Effect of Temperature on Activity of Water Quenched Slag Prepared by Reducing Iron Oxide of Steel Slag with Coal Gangue

SONG Qiang¹, NIE Jiao¹, SONG Tiantian¹, HU Yaru¹, DENG Yang², CHEN Yanxin¹, CHENG Fuan¹

(1. College of Materials Science and Engineering Xi'an University of Architecture and Technology, Xi'an 710055, Shaanxi, China;

2. Shaanxi Fuping Eco-cement CO., LTD. Weinan 711709, Shaanxi, China)

Extended Abstract

Introduction Using as supplementary cementitious materials (SCM) is one of the most important research topics in the resource utilization field of steel slag. However, the iron oxide content in steel slag is greater than that of other cementitious materials (*i.e.*, clinker, granulated blast furnace slag, and fly ash). The solid solution formed by FeO and CaO-MnO-MgO (RO phase), hematite, wustite, Ca₂Fe₂O₅(C₂F) and other Fe-bearing phases have little contribution to the activity of ground steel slag. Some researchers use reductants such as H₂, CO, anthracite, silicon carbide, and carbon powder to reduce iron oxides from molten steel slag into ferroalloys. Aluminosilicate melt is quenched and resultant residual used as SCM. These methods have a challenge of high cost of reducing agents and difficulty in industrial utilization. This paper used residual carbon in coal gangue as a reductant to reduce iron oxides of steel slag. The remaining aluminosilicate was quenched to prepare slag with a high hydration activity, which could achieve the synergistic disposal of two types of industrial solid waste.

Methods Based on the chemical composition of steel slag and coal gangue, as well as the fixed carbon content of coal gangue, the amount of coal gangue required for the sufficient reduction of iron oxide in the two raw materials was determined. After mixing ground coal gangue and ground steel slag thoroughly, the mixture was heated to 1 200, 1 300, 1 350, 1 400, 1 450 °C and 1 500 °C at 40 °C/min in an argon atmosphere (3 L/min), and then quenched with water after holding for 30 min. The resultant strip off iron particles, and the remaining aluminum silicate is called water quenched residue (WQR). The iron recovery rate was determined according to the chemical composition of the WQR. The mineral phases were determined by an X-ray diffractometer (XRD, Rigaku Co., Japan), and the glass content in water quenched residue was calculated using the Rietveld quantitative analysis method.

The paste and mortar samples were prepared by adding 30% (in mass fraction) WQR into the reference cement. The cross-sectional morphology was determined by a model GeminiSEM 500 scanning electron microscope (Zeiss Co., Germany). The elements distribution of the paste samples was analyzed. The heat release curve of hydration for the first 72 h was recorded with a model TAM-Air-8microcalorimeter (TA Instruments Co., USA). The thermal behavior of the pure slurry after hydration for 3 d, 7 d and 28 d were analyzed by a model TGA/DSC1/1600 thermogravimeter (TG, Mettler Toledo Co., USA). The mortar specimens with a dimension of 40 mm×40 mm×160 mm were used for testing flexural and compressive strength after standard curing to the specific age.

Results and discussion The reduction temperature is an important factor affecting the iron recovery rate in steel slag and the vitrification of WQR. When the reduction temperature exceeds 1 300 °C, the reduction rate significantly increases. When the temperature exceeds 1 350 °C, the Fe₂O₃ content decreases from 20% in the steel slag raw material to less than 2% in the WQR. The main mineral phases in the reduced residue at 1 100 °C are merwinite and gehlenite. When the temperature rises to 1 350 °C, the

diffraction peaks of gehlenite disappear. At 1 450 °C, the diffraction peaks of merwinite almost disappear. When the reduction temperature is less than 1 300 °C, the glass content in WQR is less than 60%. When the temperature reaches 1 350 °C, the glass increases rapidly, approaching 80%. The glass exceeds 90% with further increasing the reduction temperature to 1 450 °C. The fusion temperature is an important factor for the degree of vitrification of WQR.

The hydration heat release curve of cement paste shows that the second exothermic peak of sample prepared with WQR generated at 1 500 °C is similar to the peak of the reference cement, but the exothermic peak attributed to the formation of the second ettringite decreases. The second exothermic peak of cement with WQR at 1 400 °C is 1 mw/g lower than that of WQR cement at 1 500 °C. A lower heat release rate is due to the presence of crystalline phases in the WQR at 1 400 °C. After 72-h hydration, a higher cumulative heat of the paste prepared with WQR at a higher melting temperature occurs. The cumulative heat of WQR cement at 1 400 °C and 1 500 °C is 71.65% and 85.64% of the reference cement, respectively. This is due to the high reduction temperature leading to a high degree of vitrification, thereby improving the hydration activity of the WQR.

The XRD and TG results indicate that the Ca(OH)_2 content in the paste gradually decreases with the increase of steel slag reduction temperature and the hydration time of WQR cement. This is because the glass content and pozzolanic activity of WQR increase with the increase of reduction temperature. Consequently, the Ca(OH)_2 content of WQR cement decreases.

The strength results of the mortar show that the 3-d flexural strength of cement with 30% WQR is almost equivalent to that of the reference cement. The growth rate of flexural strength of WQR cement is higher than that of reference cement with curing time, and its strength reaches 130% of reference cement strength at 28 d. The compressive strength of WQR cement at 3 d is 60% of the reference cement. The compressive strength development rate of WQR cement is higher than that of reference cement. After 28-d hydration, the compressive strength of cement prepared with WQR at 1 400 °C reaches 90% of the reference cement strength.

Conclusions The recovery rate of Fe could reach 63%~94% by using carbon in coal gangue as a reducing agent to reduce iron oxide of steel slag. The reduction rate increased as the reduction temperature increased. When the reduction temperature was below 1 300 °C, the mineral phases of the WQR mainly consisted of merwinite and gehlenite. The crystalline phase gradually decreased as the temperature increased. When the reduction temperature was >1 450 °C, the glass content maintained at 91%. The glass phase content and the pozzolanic activity in WQR increased as the reduction temperature increased. The cement prepared with WQR had good mechanical properties. After 28-d hydration, the flexural strength and compressive strength of WQR cement reached 130% and 90% of the reference cement, respectively.

Keywords steel slag; coal gangue; carbon thermal reduction; water quenched residue; hydration activity