Effects of solid waste on the mechanical properties and hydration products of cement mortar

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Abstract. The existence of a large number of solid wastes has caused great pollution to the environment. In this study, different solid waste such as steel slag, water-quenched manganese slag, red mud and coal gangue was used in cement mortar, and the mechanical properties and hydration products were studied. Results showed that water-quenched manganese slag and high-calcium coal gangue after spontaneous combustion showed higher activity. Coal gangue has the highest activity of 102% and red mud has the lowest activity of 69%. Both steel slag and manganese slag added samples showed higher strength than that of manganese slag and steel slag separately added samples. The composite admixture of steel slag, manganese slag, red mud and coal gangue showed the highest strength at 7%, 8%, 8%, 7% and 7%, respectively.

1. Introduction

Recent years, nearly 10 billion tons of industrial solid waste is produced every year in China as economic development [1]. The accumulation of a large amount of industrial solid wastes has caused land resources to reduce, which has also caused the pollution of the environment. Environmental protection and sustainable development have become the development direction of industrial solid waste utilization. At present, the industrial solid wastes with lower utilization rates are mainly red mud, steel slag, manganese slag and coal gangue. With the improvement of China's urbanization level and the rapid development of infrastructure construction, China's cement output and usage has always ranked first in the world [2]. Cement production consumes lots of resources and causes large pollution of the environment [3]. Due to a large amount of solid waste and the large amount consume of cement, the use of solid waste to replace part of cement in cement-based material has become a problem that desperately needs to be solved.

Steel slag is a kind of waste slag produced during the steelmaking process. For every 10,000 tons of steel produced, 2500 tons of steel slag is produced. The main components of steel slag are CaO, SiO₂, Fe₂O₃, and MgO, which account for more than 80% of the steel slag composition [4-7]. China is one of the countries with abundant manganese slag resources in the world. At least 3.5 tons of manganese slag is produced for each ton of metal manganese produced. The main chemical components of manganese slag are CaO and SiO₂, and the content of both is above 55%, followed by Al₂O₃, MNO, MgO, and so on [8]. Red mud is a by-product of alumina production. The red mud production is huge as the fourth largest alumina producer in the world of China. The composition of red mud mainly includes CaO, Al₂O₃, SiO₂, Fe₂O₃ and so on [9-10]. Coal gangue is the main waste in...
the process of coal mining and washing, and its emissions are 10% to 15% of the annual output of raw coal. For each ton of raw coal produced, about 0.14 tons of coal gangue will be produced. A large amount of coal gangue discharge takes up a lot of land resources and causes environmental pollution [11-13]. The main component of coal gangue is coal-based kaolinite, whose main components are SiO\textsubscript{2} and Al\textsubscript{2}O\textsubscript{3}. After calcination at high temperatures, metakaolin with high pozzolanic activity can be formed [14].

The application of solid waste in cement-based materials and the application under synergy has attracted widespread attention of researchers. Cheng [15] et al showed a new cementitious material prepared by using waste drilling fluid, blast furnace slag, red mud and the new cementitious material was environmentally friendly and showed better performance. Zhang [16] et al prepare the road base material by using electrolytic manganese residue, red mud and carbide slag as main raw materials, excellent mechanical and durability performance obtained under synergistic action and heavy metals can be well solidified by the road base material. Study by Yi [17] et al found that the addition of coal gangue can change the chemically and physically bound chloride capability. Nath [18] et al suggested that partial replacement of cement by manganese slag reduced compressive strength at early ages and almost similar strength after 28 days curing was achieved with the control sample.

In this study, the activity, compressive strength and phase composition of cement-based materials with steel slag, manganese slag, red mud and coal gangue added were studied. The synergistic effect of those industrial solid waste was also researched and compared with fly ash added cement-based materials.

2. Materials and methods

2.1. Materials
Cement of P•O 42.5 was used in this study and which was produced by Sichuan Esheng Cement Co., Ltd. ISO standard sand produced by China National Building Materials Institute was used for cement mortar samples.

The steel slag (S) was produced from Guizhou Liuzhou Iron and Steel Plant, water-quenched manganese slag (M) was produced from Guilin Xiangyun Manganese Industry Co., Ltd., coal gangue (C) was from Junlian, Yibin, Sichuan province, red mud (R) was produced by Guangxi Pingguo Aluminum Industry, and Class I fly ash (F) was provided by Yibin Power Plant.

The steel slag, manganese slag, and coal gangue used are all ground to powder. Coal gangue is spontaneously ignited in nature.

The specific surface area of raw material after grinding is shown in Table 1. The SEM image of the powder after grinding is shown in Figure 1. It can be seen that all materials showed an irregular shape and the surface encased by smaller particles except fly ash. The enclosed with smaller particles of red mud was more obvious.

| Sample                  | SSA/m\textsuperscript{2}•kg\textsuperscript{-1} |
|-------------------------|-----------------------------------------------|
| Cement                  | 357                                           |
| Steel slag (S)           | 440                                           |
| Manganese slag (M)       | 626                                           |
| Coal gangue (C)          | 411                                           |
| Red mud (R)              | 674                                           |
| Fly ash (F)              | 340                                           |
The chemical composition of raw material is shown in Table 2. It can be seen that coal gangue has a similar composition to that of cement. Compared with red mud and fly ash, steel slag and manganese slag showed higher CaO content. Steel slag, manganese slag and red mud have similar SiO$_2$ content, and fly ash showed higher SiO$_2$ content. A large amount of Fe$_2$O$_3$ was contained in steel slag, manganese slag and red mud.

| Sample | CaO  | SiO$_2$ | Al$_2$O$_3$ | SO$_3$ | Fe$_2$O$_3$ | MgO  | MnO  | Na$_2$O | TiO$_2$ | LOI  |
|--------|------|---------|-------------|--------|------------|------|------|---------|--------|------|
| Cement | 64.91| 19.4    | 4.76        | 2.87   | 3.88       | 2.25 | 0.04 | -       | -      | 0.23 |
| S      | 44.59| 15.68   | 8.09        | 0.36   | 19.51      | 4.81 | 2.22 | 0.2     | 1.61   | 2.36 |
| M      | 43.97| 16.89   | 8.81        | 0.4    | 17.87      | 5.02 | 2.51 | 0.24    | 1.61   | 3.97 |
| C      | 64.71| 21.71   | 4.82        | 0.2    | 4.43       | 1.61 | 0.25 | 0.64    | 0.36   | 0.89 |
| R      | 15.48| 14.59   | 19.82       | 0.54   | 29.97      | 0.36 | 0.12 | 10.48   | 6.93   | 6.54 |
| F      | 5.58 | 49.27   | 27.96       | 1.13   | 8.97       | 0.9  | 0.08 | 0.73    | 2.76   | 2.31 |

XRD patterns of steel slag, manganese slag, coal gangue, red mud and fly ash are shown in Figure 2. It was found from the figure that coal gangue contains a large amount of C$_3$S and C$_2$S phases. It can be determined that the coal gangue used in this paper is coal gangue powder after self-ignite as the smaller loss on ignition (as shown in Table 2). Coal gangue reacts with some minerals at high temperatures and C$_3$S and C$_2$S phases were formed. C$_2$S phase also found in steel slag.
Figure 2. XRD spectra of raw materials

Figure 3. Particle size distribution of raw material

Figure 3 shows the particle size distribution of raw materials. Smaller particle sizes were shown by steel slag, manganese slag, and coal gangue. The larger specific surface area was shown red mud (shown in Table 1), but the larger particle size was shown in Figure 3. This could be due to the particles agglomerated of red mud.

2.2. Mix proportions and sample preparation

The mix proportions of cement paste and mortar samples are shown in Table 3. Standard sand following Chinese standard GB/T 17671-1999 [19] was used for preparing cement mortar. The cement to a sand ratio of 1:3 is used. During mixing, the raw materials were dry-mixed for one minute and then wet-mixed for another four minutes. After mixing, pastes were cast in 2 cm × 2 cm × 2 cm molds and mortars were cast in 16 cm × 4 cm × 4 cm molds. Samples were cured for 1 day at the ambient environment (ca. 25°C/60% RH) before demolding and then cured for 3, 7, 28 and 56 days in standard curing chamber (20°C/95% RH).

| Sample  | Paste w/b | Mortar w/b | Cement (wt.%) | F (wt.%) | M (wt.%) | S (wt.%) | R (wt.%) | C (wt.%) |
|---------|-----------|------------|---------------|----------|----------|----------|----------|----------|
| Control | 0.4       | 0.5        | 100           | 30       |          |          |          |          |
| F30     | 0.4       | 0.5        | 70            | 30       | 30       |          |          |          |
| M30     | 0.4       | 0.5        | 70            |          | 30       | 30       |          |          |
| S30     | 0.4       | 0.5        | 70            |          |          | 30       |          |          |
| R30     | 0.4       | 0.5        | 70            |          |          |          | 30       |          |
| C30     | 0.4       | 0.5        | 70            |          |          |          |          | 30       |
| M15S15  | 0.4       | 0.5        | 70            | 15       | 15       |          |          |          |
| M7S15R8 | 0.4       | 0.5        | 70            | 7        | 15       | 15       |          |          |
| M7S4R12C7 | 0.4    | 0.5       | 70            | 7        | 4        | 12       | 7        |          |
| M7S8R8C7 | 0.4       | 0.5        | 70            | 7        | 8        | 8        | 7        |          |
| M7S12R4C7 | 0.4     | 0.5       | 70            | 7        | 12       | 4        | 7        |          |

2.3. Test methods

2.3.1. X-ray diffraction. The raw materials and hydration products of cement paste were studied by X-ray diffraction (XRD, Bruker D8 Advance, Germany). Samples were vacuum oven-dried at 50 °C for 48 hours and then grounded into powder smaller than 75μm by agate mortar. Cu-Kα radiation was conducted at a voltage of 40 kV and an accelerated current of 40 mA. The scan speed of 0.5 sec/step and increment of 0.02° was used.
2.3.2. **SEM.** Scanning electron microscopy (SEM) was used for the microstructure of raw materials and samples were made conductive by coating platinum film of 20 nm thick.

2.3.3. **Compressive strength.** The compressive strength test of cement mortar was according to GB / T17671-1999 [19].

3. **Results and discussion**

3.1. **Activity of different solid wastes and fluidity of cement mortar**

Figure 4 showed the fluidity of cement mortars with different solid wastes. All solid wastes showed a negative impact on the fluidity of the cement mortar, and fly ash was beneficial to the modification of fluidity which contributed to the spherical of fly ash particle and the ball effect. The greatest reduction of fluidity was shown by red mud addition samples. The large specific surface area of red mud and more small particles attributed to this result. Also, the loose and porous structure of red mud might be absorbed some mixing water, resulting in a decrease of fluidity. Added of coal gangue showed the negative effects on fluidity, the reason was similar to red mud-added samples. For the compound-added samples, it can be seen that as the percentage of red mud added increases, the fluidity gradually decreases. M7S8R8C7 sample showed better effects on fluidity, which may be related to the particle accumulation between different solid wastes.

![Figure 4. Fluidity of different solid wastes added mortar](image)

The activity of different solid wastes is shown in Figure 5. The activity test method is based on the standard GB/T1596-2017 [20]. It can be seen that coal gangue showed the highest activity of 102%, the activity of other solid waste was lower than that of the control sample. Coal gangue was undergone the process of spontaneous combustion and C₃S and C₂S phases were forming, the highest activity resulted. Compared with fly ash, steel slag and red mud, water-quenched manganese slag showed higher activity of about 89%. For the activity of compound solid waste admixture, the activity could be increased under the synergistic effect between different solid waste. The activity under the mixed system of steel slag, manganese slag, red mud and coal gangue is higher than the single manganese slag, steel slag and red mud. The activity was increased with the increase of steel slag content. The compound system of solid waste also improved with coal gangue added. The high content of CaO in the steel slag and the high activity of coal gangue might be contributed to this result.

3.2. **Compressive strength**

The strength development of cement mortar with different solid waste is shown in Figure 6 and Table 4. For the sample solid waste added separately, it can be seen that coal gangue-added samples showed the highest strength when cured for 3, 7, 28, and 56d. Compressive strength of C30 samples was
higher than that of the control samples at curing time of 28 and 56d and 48.6 and 58.2 MPa was shown respectively, which was attributed to the existence of the C₃S and C₅S phases in coal gangue. M30 samples also showed higher strength with increasing curing time, and f 89% of control samples was shown when cured time up to 28 and 56d. The strength of fly ash-added samples gradually increased with the increase of curing time, and the strength was lower than that of the samples with steel slag, manganese slag, red mud and coal gangue at the curing time of 3 and 7 d. With the curing time increasing to 28 and 56d, the strength of F30 was higher than that of steel slag and red mud added samples. This result was attributed to the low reactivity of fly ash at an early age. S30 samples showed a slow strength to develop with the increase of curing time. Strength shrinkage was resulted by red mud-added samples at a late age, which might be due to the high content Fe₂O₃ of red mud and strength development was retarded.

For the compound added mortar samples, it can be seen in Figure 6 (b) that the strength of steel slag and manganese slag-added samples was higher than that of separate added samples of steel slag and manganese slag. This indicated that the reaction activity could be improved under the synergy condition. Under both added steel slag, manganese slag, coal gangue and red mud, the problem of post-strength reduction of samples only red mud-added was solved. The later strength was also improved when compared with separately steel slag and red mud added samples. This may be attributed to two reasons: the higher activity of coal gangue and manganese slag supplements the insufficient strength of steel slag and red mud; the synergistic interaction between different solid waste powder improved the activity of steel slag and red mud. M7S8R8C7 and M7S12R4C7 samples showed higher strength when compared with M15S15 and M7S15R8 samples, 45.9 and 45.9 MPa of compressive strength was shown at curing for 56 days by M7S8R8C7 and M7S12R4C7 samples, respectively.

![Figure 6. Compressive strength of cement mortar](image)

**Table 4. Compressive strength of cement mortar**

| Samples   | Compressive strength /MPa |
|-----------|---------------------------|
|           | 3d        | 7d        | 28d       | 56d       |
| C         | 32.6      | 37.2      | 47.8      | 53.0      |
| F30       | 20.9      | 26.0      | 37.4      | 44.7      |
| M30       | 25.7      | 31.3      | 42.7      | 47.3      |
| S30       | 21.9      | 27.9      | 36.6      | 38.7      |
| R30       | 25.8      | 32.1      | 32.9      | 30.2      |
| C30       | 27.0      | 36.4      | 48.6      | 58.2      |
| M15S15    | 24.8      | 32.9      | 39.6      | 45.5      |
| M7S15R8   | 23.7      | 30.5      | 39.6      | 43.7      |
| M7S4R12C7 | 23.2      | 30.2      | 41.3      | 44.3      |
| M7S8R8C7  | 26.3      | 33.1      | 38.5      | 45.9      |
| M7S12R4C7 | 25.1      | 31.4      | 41.6      | 45.8      |
3.3. Hydration phase

The XRD pattern cement paste with different solid wastes added is shown in Figure 7. For 3 days cured samples, it can be seen that the addition of steel slag, manganese slag and red mud reduces the calcium hydroxide (CH) and unhydrated tricalcium silicate (C₃S) content after hydration. The decrease in the amount of CH and C₃S could be attributed to two aspects; firstly, the partial replacement of cement reduced the amount of cement in the mixture; secondly, steel slag, manganese slag and red mud react with CH and more C-S-H gel was formed. For the coal gangue-added samples, it can be seen that the similar content of CH and C₃S was shown when compared with the control group at a curing time of 3 days. This might be due to the composition of coal gangue was similar to cement. Fly ash-added samples showed the higher CH content when compared to other samples, and lower unhydrated C₃S content was also shown. This result indicated that partial replacement of cement by FA promoted cement hydration and more CH was produced. Meanwhile, the lower activity of FA at an early age could not react with CH, the CH content was increased.

For the compounded samples, it can be seen that the combined added of manganese slag and steel slag consumed more CH than single addition samples. Both added manganese slag, steel slag and red mud samples also showed the same results. The combined added steel slag, manganese slag, red mud and coal gangue also exhibited a positive role in the consumption of CH. These results were consistent with compressive strength and activity results.

XRD pattern of cement paste curing time of 7 days is shown in Figure 7 (b). For the control samples, it can be seen that the CH content was significantly higher than that of the curing time for 3 days sample, and the unhydrated C₃S phase was significantly reduced. steel slag, manganese slag and red mud added samples showed lower CH and C₃S content. Coal gangue-added samples still contained a more unhydrated C₃S phase. The compound added sample had similar results compared to the 3 days curing time sample.

![Figure 7. XRD spectra of cement paste hydration for 3 days and 7 days](image-url)
4. Summary

In this paper, the strength and hydration products of cement mortar samples mixed with steel slag, manganese slag, red mud and coal gangue were studied and analyzed. The conclusions are as follows:

(1) For separately added samples, water-quenched manganese slag and high-calcium coal gangue after spontaneous combustion showed higher activity. Coal gangue has the highest activity of 102% and red mud has the lowest activity.

(2) The steel slag and manganese slag added samples showed higher strength than that of manganese slag and steel slag separately added samples, which indicates that the synergistic effect could improve the reactivity.

(3) The composite admixture of steel slag, manganese slag, red mud and coal gangue has the highest strength at 7%, 8%, 8%, 7% and 7%, 12%, 4%, and 7%, respectively.

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References

[1] Ren C Z, Wang W L, Yao Y G, Wu S, Qamar and Yao X L 2019 J. Cleaner Prod. 252 119840
[2] Wei J X and Cen K 2019 Sci. Total Environ. 653 200-211
[3] Liu X B and Fan Y B 2018 Energy Policy, 112 141-151
[4] Jiao W X, Sha A M, Liu Z Z, Jiang W, Hu L Q and Li X Z 2020 J. Cleaner Prod. 261 121197
[5] Shen W G, Liu Y, Wu M M, Zhang D, Du X J, Zhao D Q, Xu G, Zhang B L and Xiong X 2020 J. Cleaner Prod. 256 120244
[6] Guo J L, Bao Y P and Wang M 2018 Waste Manage. 78 318-330
[7] Jiang Y, Ling T C, Shi C J and Pan S H 2018 Resour., Conserv. Recycl. 136 187-197
[8] Xu Y T, Liu X M, Zhang Y L, Tang B W and Mukiza M 2019 Constr. Build. Mater. 229 116831
[9] Zhang J Z, Li P Z, Liang M, Jiang H G, Yao Z Y, Zhang X M and Yu S X 2019 Constr. Build. Mater. 237 117821
[10] Liu W C, Chen X Q, Li W X, Yu Y F and Yang K 2014 J. Cleaner Prod. 84 606-610
[11] Wang S B, Luo K L, Wang X and Sun Y Z Environ. Pollut. 209 107-113
[12] Li J Y and Wang J M 2019 J. Cleaner Prod. 239 117946
[13] Querol X, Izquierdo M, Monfort E, Alvarez E, Font O, Moreno T, Alastuey A, Zhuang X, Lu W and Wang Y 2008 Int. J. Coal Geol. 75 93-104
[14] Zhang Y L and Ling T C 2019 Constr. Build. Mater. 234 117424
[15] Cheng X W, Long D, Zhang C, Gao X S, Yu Y J, Mei K Y, Zhang C M, Guo X Y and Chen Z W 2019 J. Cleaner Prod. 238 117902
[16] Zhang Y L, Liu X M, Xu Y T, Tang B W, Wang Y G and Mukiza E 2019 Constr. Build. Mater. 220 364-374
[17] Yi C, Ma H Q, Zhu H G, Li W J, Xin M L, Liu Y L and Guo Y D 2018 Constr. Build. Mater. 167 649-656
[18] Nath S K and Kumar S 2016 Evaluation of the suitability of ground granulated silico-manganese slag in Portland slag cement Constr. Build. Mater. 125 127-134
[19] Method of testing cements-determination of strength, GB/T 17671-1999
[20] Fly ash used for cement and concrete, GB/T 1549-2017