IOP Conf. Series: Materials Science and Engineering **301** (2018) 012055 doi:10.1088/1757-899X/301/1/012055

Experimental Study of Goaf Filling Materials Based on Red Mud

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Abstract. Red mud as soild waste is difficult to treatment. Goaf filling materials can make a large use of red mud. By the experimental study,we find that the red mud, fly ash, ground slag and desulfida-tion gypsum can be used to make goaf filling materials based on the principle of alkali excitation and metalion stability.Through the control variable method, we find that the optimal proportion of goaf filling materials based on red mud is red mud 55%, fly ash 30%, cement 7.5%, fly ash 2.5%, desulfurization gypsum 5%, admixture 1%, and water solid ratio=1:1.2.The 28days final material strength was 2.0 MPa,which achives the technical specification requirements.Through the test of SEM, XRD and IR, it is indicated that the strength formation of goaf filling material based on red mud is from the unformed linking hydration products of amorphous alkali excitation system. With curing time from 3 to 7 days, the unformed linking hydration products grown a lot of vitreous hydration products. When hydration reaction basicly finished after 28 days, the hydration products have developed into a large volume of massive vitreous with an extremely dense structure. The Ca_2SiO_3 mineral phase is significantly reduced, which is participate in hydration reactions. The decrease of Ca_2SiO_3 indicates that the Si-O bond in the system have been ruptured and reorganized.

1. Introduction

Red mud as solid waste is generated during the extraction of nonferrous metals such as aluminum, copper etc.,and characterized by red colour due to containing a large number of iron oxide[1-2].It is estimated that every production of 1 tons of alumina, produce 0.8-1.5 tons of red mud[3-4]. The amount of red mud existing in the global has more than 200 million tons. Not only the red mud pile sites can cause great damage to the environment, occupy basic farmland, pollute soil and water, but also is a potential dangerous source of debris flow [5].Gordon et al. have used XRD scans and electron micrography to study the characterization of the red mud composites [6].They find the red mud composite suitable for construction material because of cheap and easily available. Sabat and Mohanta have stabilized red mud using fly ash as a durable material[7].Akshaya Kumar Sabat and Swapnaranee Mohanta have studied the percent swell and durability of fly ash stabilized red mud cushioned expansive soil[8]. The former research results indicated that the most effective disposal way for red mud is resources comprehensive utilization, such as preparation of cement, production of ceramic materials and extracting of valuable and rare metallic elements. But the consumption of above-mentioned utilization ways is accounted for only 3-8%, which is much less than the growing of the red mud. Therefore, it is urgent to study the methods and techniques that can consume a lot of red mud. This paper is about the utilization of solid wastes based on red mud.

2. Materials

The fly ash is selected from gangue power plant of the fifth coal mine of Yangquan Coal Industry Group, Shanxi. The pH value is 9.6, the specific surface area is 662.7m^2/kg and the percentage of 45μm screen residue by square hole screen is 11.5%.The main chemical composition is shown in Table 1, and the morphology is shown in Figure 1.

Table 1. Analysis of oxide components in materials (%)

Content / Oxide / Materials	SiO_2	Al_2O_3	CaO	Fe_2O_3	SO_3	MgO	Na_2O	K_2O	TiO_2	P_2O_5	PbO	As_2O_3	Cr_2O_3	LOI
Fly ash	27.32	20.41	17.20	4.24	7.96	2.08	0.33	0.50	0.75	0.29	-	-	-	18.62
Red mud	21.43	22.72	16.49	9.98	-	-	11.51	0.42	3.98	-	0.013	0.007	0.051	13.41
Cement	23.40	6.60	56.79	2.88	2.10	2.19	60.19	0.69	-	-	-	-	-	3.69
Ground slag	30.98	14.60	38.15	0.30	2.31	9.07	0.36	0.37	2.16	0.03	-	-	-	0.98
Desulphurization gypsum	3.30	2.22	34.40	0.47	38.66	1.33	0.11	0.11	0.08	0.02	-	-	-	19.10

The red mud is selected from Zhaofeng Aluminum Company of Yangquan Coal Industry Group, Shanxi. The pH value is 12.69 and the specific surface area is 1085.4m^2/kg. The main chemical composition is shown in Table 1, and the morphology is shown in Figure 2.

Figure 1. Fly ash

Figure 2. Original red mud

Figure 3. Desulphurization gypsum

The cement is selected from the Shanxi Yamei cement plant. The main chemical composition is shown in Table 1, and the main technical properties are shown in Table 2.

Table 2. Technical properties of ordinary portland cement

Classification	Specific surface area(m^2/kg)	Consumptive use of water normal consistence(g)	Setting time (min)	
			Initial setting	Final setting
P.O 42.5	341	130	190	285

The ground slag is selected from the Third limited company of Shanxi Hongxia architectural engineering group. The specific surface area is 503.9m^2/kg. The main chemical composition is shown in Table 1.

The desulphurization gypsum is selected from Longchuan power plant of Yangquan city, Shanxi. The specific surface area is 175.1m^2/kg. The main chemical composition is shown in Table 1, and the morphology is shown in Figure 3.

The admixture made by ourself plays an important role in regulation of rheological properties, stimulating the activity of solid waste and stable curing effect of sodium and heavy metal ions.

3. Design and Research

The experimental method is the control variable method. Referring to the<Technical specification for building (structure) foundation treatment in coal mine goaf >(GB51180-2016) [9]and the<Application technical specification for grouting material based on cement>(GB-T50448-2015)[10], combining with previous engineering experience, the following technical requirements for goaf filling materials based on red mud are put forward: ①28d compressive strength:≥2.0MPa(low-grade);②service behavior: Initial expansion degree≥290mm; 30min retention value of fluidity≥260mm; No bleeding phenomenon.

3.1. Influence of the Amount Of Red Mud

The cement quantity of fixed filling material is 7.5%, the ground slag content is 2.5%, the desulfurization gypsum content is 5%, the amount of admixture is 1% (mixed), ratio of water and solid is 1:1.2, the content of red mud respectively is 45%,50%, 55% and 60%, the rest is filled by fly ash. Than testing separately the working and mechanical properties of filling material, the results are shown in Table 3.

From the Table 3, it is concluded that the filling material properties gradually weakened with the increasing of content of red mud. When the red mud content as high as 60%, the viscosity and fluidity of red mud showed a sharp downward trend. And with the increasing of the content of red mud, the filling material strength is also gradually reduced. When the red mud content is 55%, the strength of 7d is 1.05MPa, and the strength of 28d is 2.20MPa, which meet the technical requirements of this project.

Table 3. Influence of the amount of red mud on the working and mechanical properties

Number	Admixture of red mud (%)	Specific gravity	Viscosity (s)	Fluidity (mm)	30 min value of fluidity (mm)	7d Intensity(MPa)	28d Intensity(MPa)
1-1	45	1.535	20.66	350	310	1.25	3.02
1-2	50	1.520	22.53	340	300	1.13	2.75
1-3	55	1.515	30.40	320	300	1.05	2.20
1-4	60	1.510	42.00	280	240	0.84	1.85

3.2. Influence of the Amount of Cement

The parameters of the experiment are kept unchanged; we only change the content of red mud and cement. When the quantity of red mud in fixed filling material is 55%, and the content of cement respectively is 2.5%, 5%, 7.5%, 10% and 12.5%.The results are shown in Table 4.

Table 4. Influence of the amount of cement on the working and mechanical properties

Number	Admixture of cement (%)	Specific gravity	Viscosity (s)	Fluidity (mm)	30 min value of fluidity (mm)	7d Intensity(MPa)	28d Intensity(MPa)
1-5	2.5	1.505	32.34	315	300	0.55	0.75
1-6	5.0	1.505	33.21	320	300	0.89	1.67
1-7 (1-3)	7.5	1.515	30.40	320	300	1.05	2.20
1-8	10.0	1.525	35.14	310	290	1.45	2.57
1-9	12.5	1.530	34.13	315	280	1.89	3.01

The Table 4 shows that the change of cement quantity has little effect on filling materials working performance. The viscosity of filling materials is located between 30-35s, the initial fluidity is about 320mm, and the 30min value of fluidity is about 300mm.And with the increasing of cement content, filling material strength becomes increased gradually. When the cement content are growth from2.5% to 12.5%, the 28d intensity of filling materials become increased from 0.75MPa to 3.01MPa.Considering the economy, the quantity of cement is suitable for 7.5%.

3.3. Influence of the Amount of Ground Slag

The red mud quantity of fixed filling materials is 55%, the cement quantity is 7.5%.The other parameters of the experiment are kept unchanged, we only change the content of ground slag respectively from 0%, 2.5% to 5.0%.The results are shown in Table 5.

The Table 5 shows that with the increasing quantity of ground slag, the viscosity of filling material is also increased, and the fluidity of filling material is gradually decreased, and they all meet the relevant technical requirements. With the increasing of ground slag, filling material strength becomes increased , when the content of ground slag is added from 0% to 5%, the 28d strength of filling materials is increased from 1.58MPa to 2.56MPa.Considering the less ground slag resources ,higher cost and economy, the ground slag content is suitable for 2.5%.

Table 5. Influence of the amount of ground slag on the working and mechanical properties

Number	Admixture of ground slag (%)	Specific gravity	Viscosity (s)	Fluidity (mm)	30 min value of fluidity (mm)	7d Intensity(MPa)	28d Intensity(MPa)
1-10	0	1.510	25.34	345	315	0.75	1.58
1-11 (1-3)	2.5	1.515	30.40	320	300	1.05	2.20
1-12	5.0	1.530	33.14	305	295	1.25	2.56

3.4. Influence of the Amount of Desulphurization Gypsum

The red mud quantity of fixed filling materials is 55%, the cement quantity is 7.5%,and the ground slag quantity is 2.5%.The other parameters of the experiment are kept unchanged, we only change the content of desulphurization gypsum respectively from 0%, 2.5%, 5.0% to 7.5%.The results are shown in Table 6.

Table 6. Influence of the amount of desulphurization gypsum on the working and mechanical properties

Number	Admixture of desulphurization gypsum (%)	Specific gravity	Viscosity (s)	Fluidity (mm)	30 min value of fluidity (mm)	7d Intensity(MPa)	28d Intensity(MPa)
1-13	0	1.500	25.04	350	315	0.81	1.68
1-14	2.5	1.505	28.23	330	300	0.94	1.77
1-15 (1-3)	5.0	1.515	30.40	320	300	1.05	2.20
1-16	7.5	1.520	35.14	300	260	1.01	2.10

The Table 6 shows that with the increasing content of desulphurization gypsum, the viscosity of filling material is also increased, and the fluidity of filling material is gradually decreased. When the content of desulphurization gypsum increases to 7.5%, the 30min fluidity of filling material reduced to 260mm.With the increasing of desulphurization gypsum content, the strength of filling materials becomes firstly increased and then decreased gradually. When the content of desulphurization gypsum is 5%, the 28d strength of filling material reached the highest value of 2.20MPa.

3.5. Influence of the Amount of Admixture

The red mud quantity of fixed filling materials is 55%, the cement quantity is 7.5%, the ground slag quantity is 2.5%,and the desulphurization gypsum quantity is 5%.The other parameters of the experiment are kept unchanged, we only change the content of admixture respectively from 0%, 0.5%, 1.0% to 1.5%.The results are shown in Table 7.

Table 7. Influence of the amount of admixture on the working and mechanical properties

Number	Admixture of admixture (%)	Specific gravity	Viscosity (s)	Fluidity (mm)	30 min value of fluidity (mm)	7d Intensity(MPa)	28d Intensity(MPa)
1-17	0	1.510	55.05	270	210	0.88	1.78
1-18	0.5	1.515	45.35	290	250	0.95	1.79
1-19 (1-3)	1.0	1.515	30.40	320	300	1.05	2.20
1-20	1.5	1.515	35.14	300	270	1.26	2.36

The Table 7 shows that the admixture has a significant influence on filling material, when the content of admixture is lower than 0.5%, the filling material shows higher viscosity, lower liquidity and can not meet the construction requirements. When the content of admixture is higher than 1.5%, the filling material appears bleeding phenomenon and also can't meet the construction requirements. The content of admixture has a significant influence on the mechanical properties of filling materials. With the increasing content of admixture, the strength of filling material is gradually increased. Comprehensive consideration, the content of admixture is better to 1.0%.

3.6. Influence of the Water-Solid Ratio

The red mud quantity of fixed filling materials is 55%, the cement quantity is 7.5%, the ground slag quantity is 2.5%, the desulphurization gypsum quantity is 5%, and the rest is filled by fly ash. The admixture content is 1.0%.We only changing water-solid ratio respectively1:1.0, 1:1.1, 1:1.2 and 1:1.3.The results are shown in Table 8.

Table 8. Influence of water-solid ratio on the working and mechanical properties

Number	Water-solid ratio	Specific gravity	Viscosity (s)	Fluidity (mm)	30 min value of fluidity (mm)	7d Intensity(MPa)	28d Intensity(MPa)
1-21	1:1.0	1.460	26.12	355	320	0.68	1.22
1-22	1:1.1	1.495	28.35	330	315	0.77	1.78
1-23 (1-3)	1:1.2	1.515	30.40	320	300	1.05	2.20
1-24	1:1.3	1.535	40.05	280	240	1.46	2.87

The Table 8 shows that the water-solid ratio has a significant influence on filling material. With the water-solid ratio decreases, the working properties of filling material gradually decreased. The water-solid ratio also has a significant influence on the mechanical properties of filling materials. With the water-solid ratio decreased from 1:1.0 to 1:1.3, the 28d strength of filling material increased from 1.22MPa to 2.87MPa.Therefor,, the water-solid ratio is better to 1:1.2.

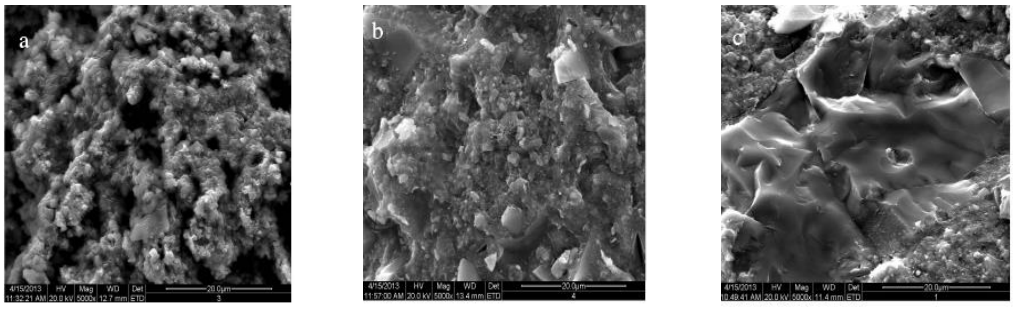
4. Discussion

According to the above control variable method, we finally determined the optimum mix proportion of goaf filling material based on red mud. It is found the optimal proportion of goaf filling materials based on red mud is red mud 55%, fly ash 30%, cement 7.5%, fly ash 2.5%, desulfurization gypsum 5%, admixture 1%, water solid ratio=1:1.2. The 28days final material strength is 2.0 MPa. The result is shown in Table 9.

Table 9. Defined proportioning of goaf filling material based on red mud

Intensity grade	Proportioning of filling materials (%)						water-solid ratio
	Red mud	Fly ash	Cement	Ground slag	Desulphurization gypsum	Admixture(mixed)	
2.0MPa	55	30	7.5	2.5	5	1	1:1.2

As we all know, the strength formation principle of goaf filling materials based on red mud mainly derived from the alkali activated system reaction product. Therefore, goaf filling materials based on red mud(material ratio， red mud: ground slag: cement: fly ash=55:2.5:7.5:35,water-solid ratio=1:1.2)are selected as the research object. In order to shield the influence of hydration products from the AFt and admixture effects, desulphurization gypsum and admixture are not included. The different ages of micro-morphology by SEM, mineral composition by XRD and infrared spectrum by IR were detected respectively.



a. maintenance for 3days **b.** maintenance for 7days **c.** maintenance for 28days

Figure 4. (a,b,c) SEM pictures of maintenance for 3days, 7days and 28days

Figure.4 shows that with the maintenance age increasing, unshaped linking structures hydration products are more and more, the sample becomes denser, consistent with the compressive strength increased with the age growth. As Figure.4a shows that when the sample maintain 3 days, many hydration products have produced and wrapped in the unreacted material particle surface with loose texture. As Figure.4b shows that when the sample maintain 7 days, a large number of vitreous body hydration products have produced, its cross-section shown smooth and compact, but due to the smaller volume of vitreous body unit, too much in quantity, more much crystal interface is easily damaged by external force, hence compressive strength is not good. As Figure.4c shows that when the sample maintain to 28 days, it can be easily observed that hydration product has developed into massive bulk vitreous body with dense structure, which indicates the hydration is basically complete.

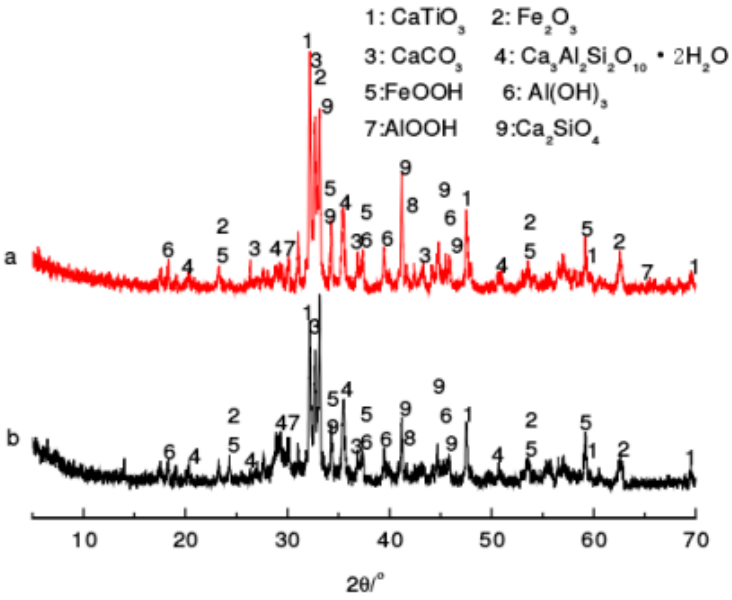


Figure 5. Analysis of XRD after maintenance for7days Original red mud; **b.** filling material based on red mud)

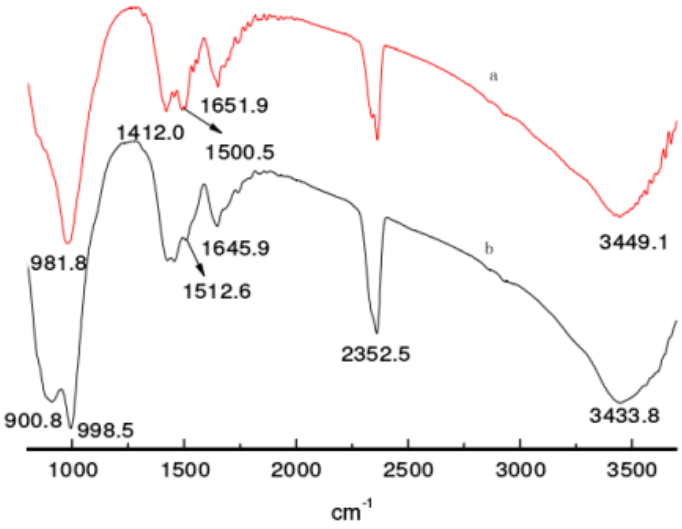


Figure 6. Infrared analysis (IR) atlas of goaf filling material based on red mud (**a.** Original red mud; **b.** Filling material based on red mud)

Figure.5 shows the analysis of XRD between original red mud and filling materials based on red mud. It can be seen that both original red mud and filling materials based on red mud have the almost same iron and calcium contained minerals, which contains $CaTiO_3$, Fe_2O_3, $CaCO_3$, $Ca_3Al_2Si_2O_{10}•2H_2O$, FeOOH, Al $(OH)_3$, AlOOH etc.mineral phase. Original red mud contains Ca2SiO3, which due to participation in hydration is significantly reduced in goaf filling material based on red mud. The hydration product of alkali activated system is mainly amorphous material based on SiO4, AlO4 tetrahedron, which is difficult to characterize the related changes in XRD.Through the decrease in the mineral phase of Ca_2SiO_3, it can be found that the Si-O bond in the system has been broken and reorganized.

Figure 6 shows that the wave numbers in infrared spectrum of red mud materials are 900.8cm^{-1}, which absorption band is four coordinated of Al-O bond. When the recombination of Al-O event occurred at the break site under the action of alkaline activator rupture and -Si-O-Si (Al) - chain structure taken shape,998.5cm^{-1} is the absorption band of -Si-O-Si (Al)-.The peak of 981.8cm^{-1}stretching vibration, alkali activated cementations materials for Si-O-Si (Al) stretching vibration absorption peaks,1645$cm^{-1}$and 1651cm^{-1} are O-H in 3433cm^{-1} And two frequency doubling peaks of 3449cm^{-1} stretching vibration. 1412cm^{-1} may be the absorption peak of C-O bond, which indicates that carbonization of alkali activated red mud cementations material is exposed in air.

5. Conclusion

Through the experimental research, it is found that the large quantity of red mud, fly ash, desulfuration gypsum can be used to make the goaf filling materials.And through the control variable method, it is also found the optimal proportion of goaf filling materials based on red mud: red mud 55%, fly ash 30%, cement 7.5%, fly ash 2.5%, desulfurization gypsum 5%, admixture 1%, water solid ratio=1:1.2.

The optimal proportion of goaf filling materials based on red mud is used to test its workability and mechanical properties, which is found that all work of performance and mechanical properties of filling material based on red mud meet the requirement of material strengt. The 28days final material strength is 2.0 MPa,which achieves the technical specification requirements.

Through the test of SEM, XRD and IR, it is indicated that the strength formation of goaf filling material based on red mud is from the unformed linking hydration products of amorphous alkali excitation system. With the curing time from 3 to 7 days, the unformed linking hydration products grow a lot of vitreous hydration products. When the hydration reaction basicly finished after 28 days, the hydration products has developed into a large volume of massive vitreous with a extremely dense structure. It is also found that the Ca_2SiO_3 mineral phase in the filling material based on red mud was significantly reduced, which is participate in hydration reactions. The decrease of Ca_2SiO_3 indicates that the Si-O bond in the system has been ruptured and reorganized.

6. Acknowledgments

This paper supported by the 2016 annual major science and technology projects of Shanxi Province'the coupling of coal ash and industrial by-product gypsum to prepare super high strength building materials technology (Item No. : MC2016-02/5)'and the laterally research 'research and development of key technologies of building a road based on red mud (Item No. : YQYT2017-01)'.

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