MULTIPURPOSE USE OF SHALE ASH AND ITS PARAGENETIC MINERAL IN CHINA

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ABSTRACT

In this paper, the ways of multipurpose use of retort residue in Shale Oil Plant, overflow and fly shale ash in power plant and paragenetic mineral of oil shale in Fushun of Liaoning Province and Maoming of Guangdong Province, the two China oil shale industry bases, are summarized and some producing problems concerned and the new researching results are introduced.

INTRODUCTION

It is known that the oil shale industries between China and other countries are different in the multipurpose use of shale ash and paragenetic minerals.

(1) The quality of oil shale source in China is lower than those in U.S and U.S.S.R. The retorting semi-coke reach to 70% and over. The amount of abandoned ash is 10 times of coal power plant. So it influences on the economical benifits .

(2) The both oil shale minerals in Fushun and Maoming ase clayey shale containing kaolinite as its main compositions. Such shale ash is different from the calicium shale ash in U.S andU.S.S.R and it does not bonding in situ abandoned and the granulated ash has heavy pollution to the atmosphere and groundwater.

(3) At present, beeause the oil shales are mined openly in China,

the large amount of paragenetic minerals in covering layer must be mined simultaneously and taken away.The praduction cost is increased. From above viewpoints,how to use the shale ash and shale paregenetic has great effects to the economy and environment benifits in China's oil shale industry.The industry units and plants concerned in China have been paid more attention to the multipurpose use of oil shale and shale paragenetic mineral for tens years.A lot of technologies for producing construction materials etc.hove been developed and achieved better benifits in economy,environment and society.

The major ways of multipurpose use which have been developed are,

1.Making Portland Cement with Shale Ash instead of Clay

Utilizing retort residue to make portland cement instead of clay have been carried out by Fushun Cement Plant and Construction Materials Division of Maoming Petroleum Industry Co.ect for serveral tens years .Now 18% retort residuce is add to the raw materials instead of clay for producing 525 grade Portland cement in Maoming Petroleum Idustry Co.A complate techiques for producing 625 grade of portland cement with overflow ash taken from boiling furnace instead of clay have been developed by Second Refinery of Fushun Petroleum Chemical Co.and Engineering Construction Institute of Petroleum Idustry ministry. So it has brought obvious economical benefits for the cement industry because the stable and cheap silicaaluminous materials can get from local place and the clay minerals can be saved.

2.Making Cement Admixture with Shale Ash

Both Fushum and Maoming oil shales are clayey shale which contains more than 85% kaolinite. Such kaolinite mineral can be decomposited into silica-alumina oxide with pozzolanic activity by dehydrating at 600℃ and over. So various tecnical ways can be dveloped for producing cement admixture,

(1)Producing admixtures with retort residue

The retort residue abandoned from Fushun and Maoming has pozzolanic activities after oxidative spontaneous combustion. These kins of ash have been used in cement industry, such as adding 10% reburnt retort residue into the ingredient for making portland cement, adding

less than 30% reburnt retort residue for making portland-pozzolana cement etc. Now, it has very popular to do this .The new activating tecnology that the retort residue is piled seperately and then reburned can increase the compressive strength ratio of pozzolanic activity of the shale ash to more than 70% and expand the usage amount of shale ash. It is developed by Maoming petroleum Co. and Engineering Construction Institute of Petroleum Industry Ministry.

(2) Making cement admixture with boilling furnace ash.

A complete technique used for producing 625 grade ordinary portland cement with 10% overflow ash and 525 grade portland-pozzolana cement with 30% overflow ash are developed by Second Oil refinery of Fushun Petrochemistry CO. and Engineering Construction Technology Institute of Petroleum Industry Ministry.

Based on the relationship between the burning parameter of boiling furnace and the activation of the ash developed by Maoming Petroleum CO. and Engineering Construction Technology Institute of Petroleum Industry Ministry, the burning temperature in boiling furnace should be controlled at 850-950℃ and the technical index of boiling furnace ash used for producing portiand-plzzolana cement admixture is provided.

(3) Making cement admixture with suspension furnace ash.

The research work on pozzolanicity of shale ash from suspension furnace has been carried out by Engineering Construction Technology Institute of Petroleum Industry Ministry. There are 3 steps on dust collecting procedure, 1 is setting chamber; 2 is cyclone ; 3 is electric dust catcher. The main technical parameters of furnace ash from -3 steps are as following, the main particle size $\leqslant 0.15 \sim 0.08$mm; loss on ignition 3.33～4.37%; specific surface 18900～20100cm²/g; bulk density 647～362g/l; compressive strength ratio of pozzolanicity 75～72%. The reseached results show that the shale ash from suspension furnece is also the high quality pozzolanic admixture.

3. Making Ceramsite with Shale Ash or Paragenetic Green Shale.

Ceramsite, or lightweight aggregate, is a new type of construction material for its light weight, high strength and multi-functions, and it has been more widely used in recent years.

(1) Producing lightweight ceramsite with shale ash.

The shale ash ceramsite with Maoming retort residue are produced by Engineering Construction Technology Institute of Petroleum Industry Ministry and Maomirg Oil Co.The research indicated that it cantains richer ferric oxide and residual kerogen .It is a good raw material for making lightweight ceramsite.The technical process must be of "grinding and granulating" ; "decarbonation at low temperature" and"fast sintering at high temperature ".The sintering temperature is at 1220℃-1250℃ .The super light ceramsite can be used for producing thermal insulation conerete which has 1000kg/m³ density and 5-7.5MPa strength.The high strength ceramsite can be used for producing 1700kg/m³ bulk density and 30MPa high strength structural lighweight conerete.

(2) Producing lightweight aggregate with green shale.

"Green shale" belongs to cover-layer shale which is paragenetic with cool and oil shale in Fushun West Open Mine、It is the almost pure shale.As it contains ferro-oxide with green colour,it is called "green shale" .The ceramsite plants have been set up and can producemore than 100,000m³ ceramsite per year.

Besides producing construction materials with the green shale in Liaoning and Beijing ect ,it is also widely used as heat- resistance liner of whole country′s petrochemistry equipments,such as regrator of catalytic equipments of oil refinery and settling equipment, because it has less than 500kg/m³ bulk density,excellent thermal insulation and high temperature resistence properties.

4.Producing Bricks with Shale Ash and Shale Paragenetic Mineral.

Utilizing 4 kinds of local industry drosses,green shale,retort residue,fly ash,coal gangul,the First Brick plant in Fushun produce internal firing bricks without any clay and fuel.the bricks are 20% lighter than normal clay bricks and have good thermal insulatian property. At present,there are 2 plants that can produce 100 million bricks per year in Fushun city ,and anothe r production line is plan nned.

Acording to the statistics made by local authorities,the production of 100 million pieces of shale bricks can make use of 250,000 ton dr-

oses and it can save 20,000ton coal,100.acres of land and several million of yuan(Renminbi)investiment.Another paragenetic mineral "shale soil" and "black mud" from the opn oil shale mine are also used for producing internal firing brick without any clay and fuels in the Brick Plant of Construction Mterials Co.of Maoming Petroleum Idustry Co,The so called "shale soil" is a poor quality shale just like soil , "black mud" is a shale just like mud .Because those shale paraganetic minerals contain suitable mineral composition and fixed cabon, the brick production cost is lower and the quality is better.

5.Filling Abandoned Workings with Shale Ash

There is a famous coal mine in Fushun. The abandoned workings must be filled with a large amount of clayless、non-firing、light weight、local materials in order to avoid roof caving and fire disastet.The retort residue already meet the following requirment, water permeability can reach 80% in 1/2munites,saturated water content can decrecse 7.5% and below,the silt only possesses 6.14%,the bulk density is only 1.1t/m³,specitic gravity is 1.7 etc.It has a lot of benifets for the pipeline transportation,compact filling,fire protection and mud cleaning etc.Now,all abandoned workings of Fushun are almost using up the retort residue got trom First and second Oil Retinery.Utilizing shale ash to filling the abardoned workings has more benefits for both coal mine amd shale Oil plant in the scope of economy,enviroment and soiety.

Additionally the silicate architectural products with shale ash and lime,ceramic raw materials and plastic filler with shale ash are produced in Maoming district.Using shale ash for making the filler of magnisite products,using green shale for making shale cotten,further used for manufacturing paper,sound absorbting materials,thermal insulation materials,reinforced plastics,reinforced magnisite ect are carried out by Fushun district. At present,some new ways for multipurpose use of shale ash and shale paragenetic have being researched continuously.

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