ABSTRACT: India produces large quantity of waste by-products from various agro industrial processes. Among these waste, utilization of phosphogypsum, fluorogypsum, slag, fly ash, lime sludges, etc. is paramount due to their enormous availability and the pollution of the ground water likely to be caused by their unplanned dumping on the fertile land. The utilization of waste gypsum particularly phosphogypsum (PG) and the fluorogypsum (FG) is significant. Unlike PG, the utilization of FG, a waste of hydrofluoric acid industry is also important as it too creates pollution of the atmosphere and the ground water. Investigations accomplished at the CBRI showed that useful cementitious binder can be produced by blending small quantity of Ca(OH)2 and chemical additives with the FG followed by fine attrition. Data showed that a plaster/binder of low water demand, high compressive strength and low water absorption can be produced. The hydration of binder as evaluated by differential thermal analysis (DTA) showed rapid conversion of anhydrite phase into dihydrate gypsum. The addition of 15-20% waste lime sludge may add economy to the new binder. The FG binder is suitable for making building bricks, flooring tiles and plastering which may be considered a new concept to the effective use and disposal of FG waste to accrue economy to the HF industry as well as to the Nation. Cost wise the FG binder is cheaper than the lime and cement binders. The technology of high strength plaster from FG and its use in making flooring tiles has been commercialized.

KEYWORDS: Phosphogypsum, fluorogypsum, slag, fly ash, lime sludges

I. INTRODUCTION

Huge quantity of wastes are being produced from the industries like metallurgy, petrochemicals, fertilizers, paper and pulp making per annum in India. From the building materials angle, the utilization of fly ash, slags, phosphogypsum, fluorogypsum, press mud, red mud etc. is paramount. Over 6.5 million tonnes of by-product gypsum are produced annually from several phosphatic and hydro-fluoric acid industries in India, Singh1. The waste of phosphoric acid industry popularly called as phosphogypsum is available to great extent. Fluorogypsum a waste of hydrofluoric acid manufacture has been studied for use in supersulphated cement or binding agents as reported by Taneja, et.al2, Swanski3. In China Republic, similar cementitious binders based on fluorogypsum were developed by Yan et.al4-5. The use of fluorogypsum which is available to the extent of slightly over 1.0 million tonne per annum is significant. Fluorogypsum contains impurities of fluoride and free acidity. These impurities particularly free acidity may interfere with the setting and strength development of plaster/building components. Since the utilization of fluorogypsum is limited, thus, there is a disposal problem of this waste and it has become essential to suitably utilize the material in value added building materials. Researches 6-9 have shown that water-resistant binding materials can be produced from phosphogypsum, slag, cement, fly ash and lime sludge. In this paper, investigations undertaken to characterize and to beneficiate fluorogypsum to make high strength binding/cementitious plaster have been presented. Effect of various chemical activators/additives on setting, strength, water absorption, porosity, etc. of the fluoro plaster/binder has been studied. The hydration and microstructure properties of the binder are reported. The suitability of fluorogypsum plaster for making building bricks and blocks containing various admixtures and its use in plastering work has been discussed. The economy of making the plaster is also indicated.
II. MATERIALS & METHODS

The sample of fluorogypsum was collected from M/s Navin Fluorine International, Bhestan, Gujarat, India. It was analyzed for chemical composition as per IS: 128810 and as per standard test procedures cited by Scott, et.al.11-12. The fluorogypsum contained Fluoride 1.32%, SiO2 + insoluble in HCl 0.65%, Al2O3 + Fe2O3 0.65%, CaO 41.19%, MgO Tr., SO3 56.10 % and Loss on ignition 0.61% and pH 5.0. Data showed that fluorogypsum possess high purity i.e. CaSO4.2H2O besides fluoride as the major impurity. The low pH value shows presence of free acidity. Minor earthly impurities of SiO2 and Al2O3 + Fe2O3 have also been identified.

The chemical activators of laboratory grades ranging from sulphates to chloride of alkali and alkaline earth hydroxides were used to activate hydration of fluoroanhydrite. Differential thermal analysis (DTA) (Stanton Redcroft, UK) and Scanning electron microscopy (SEM LEO 438VP) of the raw gypsum and hydrated plaster were studied. DTA (Fig. 1) shows endotherm and exotherm at 140° and 250°C due to the inversion of poorly weathered anhydrite into hemihydrate (CaSO4.½ H2O) and anhydrite (CaSO4 (II)) peaks. The SEM of fluorogypsum sample (Fig. 2) shows majority of crystals in fluorogypsum are anhedral to subhedral platy prismatic interspersed with lath in the jumble form. Twinning of some of the crystals may also be recorded.

III. PURIFICATION OF FLUOROGYPSUM

As the fluorogypsum contains free acidity which may corrode the grinding media (balls etc.) and the lining of the ball mill and sometimes the plaster/binder may become hygroscopic, it is therefore, essential to neutralize the acidity to get the suitable product. With this objective, effect of addition of dry hydrated lime (Ca (OH)2) was studied on the pH of fluorogypsum. It was found that at 0.8 - 1.0% addition of (Ca(OH)2) to the fluorogypsum, a neutral pH value of 7.0 was obtained. The SEM of purified fluorogypsum is shown in Figure 3. It can be seen that gypsum crystals are euhedral platy prismatic and lath shaped in nature without agglomeration/jumbling showing absence of any foreign impurity.

IV. RESULT AND DISCUSSION

Properties of Flooring Tiles The properties of flooring tiles moulded from polymerized and activated FG are listed. It can be seen that the phosphogypsum flooring tiles complied with the requirements of flexural strength, water absorption and wear resistance as given in IS: 1237-1980.

The tiles produced using fly ash or red mud in place of pigments also complied with the standard requirements. These tiles are suitable for use in flooring for general purposes for places where light loads are taken up by the floor such as office buildings, schools, colleges, hospitals and residential buildings. A typical photograph of flooring tiles produced out of anhydrite binder.
Cost Economics of the Flooring Tiles

The cost of a plant of capacity 100 m²/day FG tile may cost the capital investment of 30-35 lakhs. The major equipment required for the plant may be blender, ball mill/pulverizer, vibro press, demoulding plates, casting moulds, powder mixers, driers, curing chamber, etc. These plant & machinery are easily available in Indian market. Some machineries are the proprietary items. An Indian Patent entitled ‘A Novel High Strength Plaster Composition and Flooring Tiles Made Therefrom’, Patent No. 696/Del/2000 by Dr. Manjit Singh & Dr. Mridul Garg has been claimed.

V. CONCLUSION

High strength plaster can be developed from fluorogypsum waste. A mixture of Chemical activators like Ca(OH)₂, CaCl₂ and Na₂SO₄ has been finalized as the strengthening compound to invert waste anhydrite into strong gypsum matrix at faster pace. The addition of 15-20% lime sludge to the binder can economize the production of fluorogypsum plaster without sacrificing the strength value. Building bricks can be produced by adding an optimum quantity of saw dust (10%), rice husk (5%) or exfoliated vermiculite (15-20%) to the fluorogypsum binder. The fluorogypsum on admixing with river sand, lime sludge and the exfoliated vermiculite (in optimum proportion) is suitable for plastering (Finish & undercoat) over the internal brick wall. The fluorogypsum plaster/binder may replace different type of cement/lime based putties available in the market. The fluorogypsum plaster is also suitable for making building blocks when mixed with washed saw dust and foamed slag for insulative purpose and light weight partitions in normal as well as multistoried buildings.

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