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Development of Photoluminescence White Cement Based Materials and Physic-Mechanical Study

Christian Gómez Solís[1], M. Vallejo[1], M. Sosa[1],
J. Jesús Bernal Alvarado[1], T. Fraga[1], G. Fajardo[2],
L.M. Torres-Martínez[2]

[1] Universidad de Guanajuato,
División de Ciencias e Ingenierías,
Mexico

[2]Universidad Autónoma de Nuevo León,
Facultad de Ingeniería Civil,
Mexico

lienquidremo@hotmail.com

Abstract. In this paper, they were fabricated cement-based mortars with photoluminescent properties, using a white cement Portland within $SrAl_2O_4$: Eu, Dy as additive, furthermore the study of mechanical properties was carried out. The photoluminescent mortar was characterized by XRD, SEM, DTA and PL spectroscopy. The XRD analysis results showed the presence of portlandite, tetracalcium aluminate hydrate, calcite and silice phases. Moreover, from the DTA analysis it was found that the $Ca(OH)_2$ reacts with the additive in a hydration reactions. Additionally, the compressive strength for samples M1 and M5 it is reduced by 8.5 and 14.9% respectively, after 28 day of curing.

Keywords: photoluminescent properties, white cement, $SrAl_2O_4$: Eu, Dy.

1 Introduction

Today the concrete industry innovation is increasing according to the needs of humanity, although it has been considered a conservative and bit innovative industry. However, several studies have been conducted focused on modifying certain characteristics that may affect concrete properties; the developments in the building materials have shown that the application of nanotechnology can improve the properties of traditional construction materials [1, 2].

The concrete is the main material of the construction industry, is one of the most versatile and useful, also where the most important technological advances are developed.

Different types of cement are manufactured with different physical, chemical properties which mainly affect the mechanical properties, which depend on the type of structure and which are to be used [3]. But, concrete has some undesirable characteristics such as, poor visual appearance. Ordinary Portland Cement is the material that gives the concrete dark gray which can be seen as a bit flashy aesthetic and monotone color.

Therefore, it is considered that the use of white cement manufacturing concrete structures makes them more appealing and beautiful, presenting very similar to gray cement mechanical properties [4].

Moreover, white cement can be distinguished from ordinary Portland cement that has low content of iron and manganese oxide, maintain special care during manufacturing and particularly grinding process performed carefully for maintainer a white color. White cement is mainly used for architectural concrete facades, for the manufacture of precast concrete and mortars cast-in-place.

White Portland cement is mainly used in the manufacture of prefabricated walls, cladding panels, terrazzo surfaces, stucco, cement paint, tile grout and decorative concrete, using additives to a certain color, however the presence of these additives that are mostly metal oxides cause changes in fresh mortar and segregation of oxides which generates spots on the materials surface [5].

Therefore, innovation to improve the properties and presentation of concrete is of great importance, mainly using photoluminescent mineral additives, which may be mixed with white cement to form concrete photoluminescent that can be used in architectural facades, roads and strips airport security, etc. Some of these mineral additives with photoluminescent properties are alkaline earth aluminates MAl_2O_4 (M = Ca, Sr, Ba), which are doped with rare earths such as Eu^{2+}, Dy^{3+}, Sm^{3+}, these materials shown high luminescence, long life time, also that emit in the visible spectrum [6,7].

These aluminates have important industrial applications, for example, use in fluorescent mercury lamps and screens of some electronic devices [6]. The aluminate-based phosphors have better properties than conventional phosphors such as sulfides, such as good chemical stability, non-radioactive, some have a longer residence time of the emission of light [8-10].

Furthermore, aluminates have applications in concrete structures, such as strontium aluminate has been used as cementing material because of its nature and its hydraulic performance, but some are more difficult to use as the aluminate barium because of their solubility water. Using this type of aluminates can improve resistance to thermal shock, resistance to environmental pollutants [11].

Furthermore, the use of aluminates favors concrete properties, improved penetration resistance chloride, possibly due to the formation of a layer of material formed by reaction with aluminate cement hydration products. And greater resistance too early and increasing the amount of aluminate can reduce the amount of heat of hydration released [12].

This paper focuses development of portland cement-based material with photoluminescent properties, using as an additive strontium aluminate doped with europium and dysprosium. Furthermore, the effect of strontium aluminate in physicochemical and mechanical properties of this composite material was studied.

2 Experiments

2.1 Synthesis of Strontium Aluminate doped Dy, Eu

In a flask quartz reactor (500 mL), stoichiometric composition of aluminum nitrate ($Al(NO_3)_3$), strontium nitrate ($Sr(NO_3)_2$), dysprosium nitrate ($Dy(NO_3)_3$) and europium nitrate ($Eu(NO_3)_3$) were dissolved 0.15 mol of acetyl acetone together with 0.26 mol of ethanol. The mixture was stirred and refluxed until temperature reached 70°C.

Then, 1 mL of nitric acid was added and the flask immediately placed onto hot plate at 180°C. The powder was introduced into a muffle furnace and maintained at 500°C. The resulting material fine powder obtained was called photoluminescence additive (PA).

2.2 Mortar Sample Preparation Using PA

A commercial white Portland cement compound [13] and standard silica sand [16] were used for the fabrication of the mixtures. The composition of mortar mixes was in according to ASTM C 109 [14], using a ratio of cement: sand 1: 2.75 and a w/c of 0.485. The PA additive was used instead of 0, 1 and 5% (by mass of cement). A total of three mortars mixes were prepared including a control mixture according to the Table 1. In order to evaluate the effect of the use of the additive on fresh properties, it was given the fluidity according to ASTM C 230 [17] and ASTM C 109 [14].

To determine setting time's pastas (ASTM C 191) [18] they were prepared achieving normal consistency (ASTM C 187) [19] first. With the proportions indicated above, they were manufactured mortar cubes 50 x 50 x 50 mm) in according to ASTM C 109 [14]. The compressive strength of the cubes was determined in triplicate at 7 and 28 days of standard curing.

2.3 Physic, Chemical and Mechanical Characterization

2.3.1 Structural, Morphological and Optical Properties

The photolumiscence of mortars obtained was characterized by X-ray powder diffraction (XRD) using a Bruker D8 Advance diffractometer with CuKα radiation ($\lambda = 1.5406$ Å). Morphology was determined by Scanning Electron Microscope (SEM) from a JEOL 6490 LV; prior to the analysis, the powder was stuck to carbon tape attached to an aluminum sample holder and then placed into the SEM chamber.

The room temperature photoluminescence (PL) spectra of mortar were carried out at Cary Eclipse Fluorescence spectrophotometer (Agilent Technologies) with an excitation wavelength of 370 nm.

The differential thermal analysis and thermogravimetric (DTA/TGA) analysis was measurement using a SDTQ600, TA Instruments apparatus at a heating rate of 10 $°C \cdot min^{-1}$ under air flow.

Table 1. Chemical composition of White Portland cement.

Component	Weight (%)
Na_2O	0.359
Al_2O_3	3.212
MgO	0.907
SiO_2	15.621
SO_3	3.903
K_2O	0.254
CaO	75.425
V_2O_5	0.017
TiO_2	0.086
MnO	0.019
Fe_2O_3	0.196
Total	99.999

2.4 Mechanical Properties

2.4.1 Fresh Mortar Testing

Flow tests were developed on mortars and normal consistency and setting times on pastes. All tests were conducted respectively in accordance with ASTM C 230 [17], ASTM C 187 [19] and ASTM C 191 [18].

2.4.1 Hardened Mortar Testing

The compressive strength was evaluated in standard cubes specimens (50 mm x 50 mm x 50 mm), based on ASTM C 109 [14] at 7 and 28 days of curing.

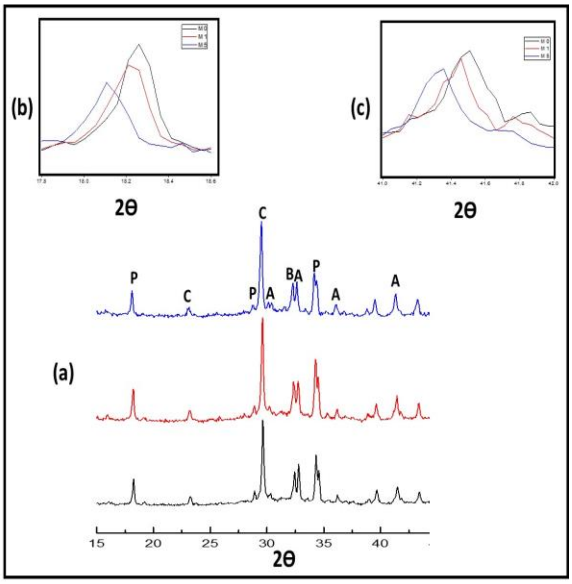

Fig. 1. XRD diffractograms for M0, M1 and M5 samples. P= portlandite, A= tetracalcium aluminate hydrate, C= calcite, S= Silice.

3. Results and Discussion

3.1 Structural and Morphological Characterization of Samples

In Fig. 1, we show the XRD patterns obtained from the M0, M1 and M5 samples. The major materials hydrated products detected by XRD was portlandite, calcite, tetracalcium aluminate hydrate and silice materials.

For M0 sample peaks calcite (2θ=29.4°), portlandite (2θ=18°) and tetracalcium aluminate hydrate (2θ=21.6°) was identified. On the other hand, in the sample M1 can be identified the same peaks as shown in M0, however an increase in the peak (2θ = 21.6 °) which corresponds to tetracalcium aluminate is hydrated.

This could be attributed to the limestone reacts more easily with the additive PA, which does not allow reacting aluminates present in the cement reactions easily. The M5 sample exhibits the greatest amount of hydrated tetracalcium aluminate, this is because the amount of $SrAl2O4$: Eu, Dy is higher and reacts with a larger amount of limestone, probably reducing the formation of the hydration products and phase CSH.

The microstructural studies performed by SEM-EDX on the M0, M1, M5, samples, are shown in the Fig. 2.

The formation of some products, which were derived from the interaction between the hydrated cement, limestone and additives PA are evidenced. Micrographies of the M0 sample Figure 2(a) shown the calcium hydroxide and particle shaped probably formed for the reaction between de PA and cement matrix. The EDX analysis of this sample showed the Ca, Si, and Al in major quantities. A similar microstructure was

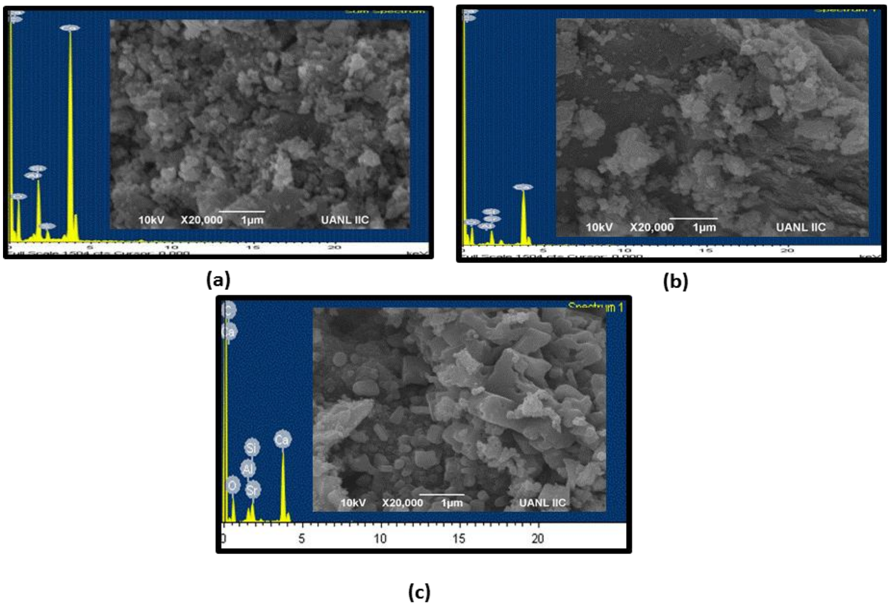

Fig. 2. Morphology of the hydration products of (a) M0, (b) M1 and (c) M5.

observed in M1 sample with 1 % of $SrAl_2O_4$:Eu,Dy Figure 2(b), irregular shape hydration products was produced after de 28 days, and small amount of large prismatic crystal are formed, due to the reaction between $SrAl_2O_4$:Eu,Dy and hydrates cements.

In EDX analysis, the presence of Sr is observed, confirming that the strontium aluminate is present in cementations matrix, which was used as an additive to generate photoluminescent concrete. In Figure 2 (c) can be see the presence of a mayor amount of large prismatic crystal, due to the mayor concentration of $SrAl_2O_4$:Eu,Dy, that can be react with a limestone and hydrates cements products, which can be corroborated with EDX analysis, where a greater amount of strontium was observed.

3.2 DTA Analysis

Figure 3 presents the DTA of samples taken from M0, M1 and M5 mortars, the thermograms of M0 showed an endothermic peak near 125 °C, which can be attributed to the partial dehydration of hydrated products formed.

An endothermic peak of calcium hydroxide can be seen between 450-550 °C. As the strontium aluminate content increased there was a reduction in this $Ca(OH)_2$ peak probably due to the hydration reactions and dilution effect.

The DTA curve shown that in sample M1 and M5 the calcium hydroxide was consumed during the reaction with a strontium aluminate, because there were a small peaks attributed to dehidroxylation of $Ca(OH)_2$ (T= 500-600 °C). The decomposition of calcite showed an endothermic peak in the range 700-900 °C, which was more prominent in white Portland cement due to the content of limestone filler.

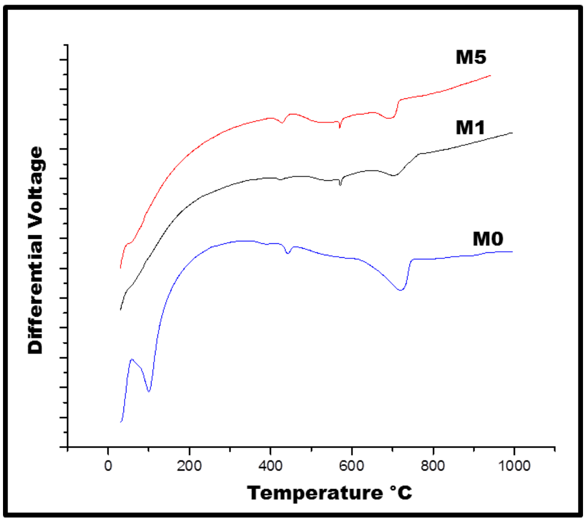

Fig. 3. DTA thermograms for concrete photoluminescence.

3.3 Emission Spectra of Mortar Photoluminescence

The emission (exited at 365 nm) spectra at room temperature of mortar photoluminescence using $SrAl_2O_4$:Eu, Dy, prepared by a solvo-combustion method are shown in Figure 4. It is observed that the emission is a symmetrical band at (470-516nm), which is attributed to typical $4f^6 5d^1 \rightarrow 4f^7$ transition of Eu^{2+}.

It is well known that in SrAl2O4: Eu^{2+}, Dy^{3+} phosphor, Eu^{2+} ions are the luminescent centers, the photo-excited luminescence is considered to be due to the transition from 5d level to 4f level of Eu^{2+}, and holes in the traps are responsible for the long afterglow. Mortar containing 5% of aluminate shows a greater emission in the visible range.

3.4 Mechanical Properties

3.4.1 Fresh Tests

The result of flow rate and setting times of the three different mortars is showed in the Table 2. This shows the effect to maintain the W/C ratio set, considering ASTM C 109 of 0.485. Obtaining the reference mortar exceeds the upper limit of the range determined by the standard by 2.5%. While, for M1, M5, with 1 and 5% additive mortar flow values are within the standard ASTM 115 and ASTM 106 respectively, which provides to mortar a workability and can be used without any problem.

Moreover, the effect of additive in the samples M1 and M5 on the setting time was studied in the mortars. When compared with M0 reference mortar (without PA), the results show that the initial setting time of 12 and 22 minutes to M1 and M5 delay, respectively. While final setting time 40 and 49 minutes setting, these times are within the ASTM C 150 in a range from 45 to 375 minutes. The additive $SrAl_2O_4$: Eu, Dy

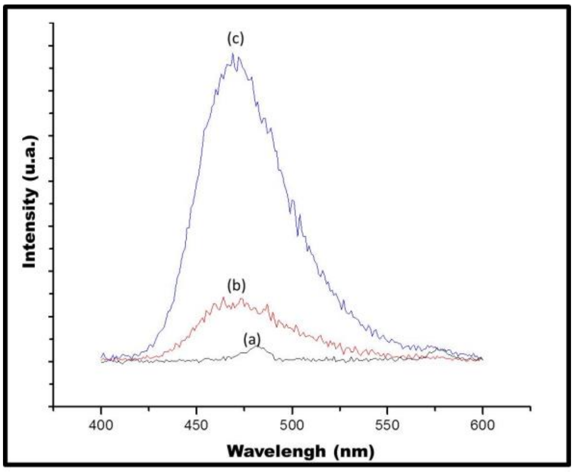

Fig. 4. Emission spectrum of the concrete photoluminescence, exited at 365 nm, (a) Mo, (b) M1 and (c) M5.

Table 2. Mix Proportion of mortars.

Sample	Cement (g)	Sand quartz(g)	Water (g)	PA (%)
M0	500	1375	242	0
M1	495	1375	242	1
M5	475	1375	242	5

changes the reaction kinetics of Portland white cement, initially accelerates and then slows, possibly interaction wetting $SrAl_2O4$: Eu, Dy and hydrates cements. The results are within the limits of the norm for a typical mix mortar.

3.4.2 Tests in The Hardened State

Figure 5 shows the compressive strength results of the mixtures. The use of $SrAl_2O_4$: Eu, Dy additive caused a decrease of compressive strength of about 5.5% and 16.6 % para M1 and M5 after 7 day and of about 8.5 % and 14.9% after 28 day.

This effect on the decreased resistance may be due to two causes. First, by adding the additive SrAl2O4: Eu, Dy replacing an amount of cement in the mix reduces the amount of clinker, reducing the amount of hydration products.

Furthermore, as shown in Fig. 1, the additive reacts with the hydration products of cement, avoiding the reaction of tetracalcium aluminate hydrate decreasing the amount of CSH formed. However, the reduction in resistance is not significant which indicates that concrete can be prepared with photoluminescent properties to 5% of additive.

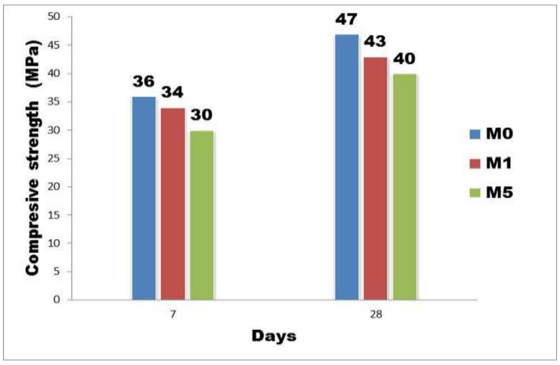

Fig. 5. Compressive strength results.

The set of results indicate that this composite material could be used in the case of a plaster or as precast concrete retaining walls for highways, borders, airports, and other applications taking advantage of light emission in dark areas or little natural or artificial lighting. The resulting product may be considered as Hi-Tec by the advantages and properties added to conventionally cement based materials.

4. Conclusion

The experimental study was conducted on the effect of additive $SrAl_2O_4$: Eu, Dy in white mortar cement-based, for a particular photoluminescent mortar which can be used in architectural structures or roadways. The material $SrAl_2O_4$: Eu, Dy can be used as additive for the manufacture of mortars phosphorescent. On the other hand, the optimum amount of additive is 5% where the best light emission observed and properties are not affected and they are within the standard for the manufacture of mortars.

The compressive strength for samples M1 and M5 it is reduced by 8.5 and 14.9% respectively, after 28 day of cured. It is necessary to continue investigation using different aluminates as additives.

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