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CRI TECHNOLOGY DIGEST

CEMENT RESEARCH INSTITUTE OF INDIA

TECHNOLOGY OF COLOURED CLINKER MANUFACTURE

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INTRODUCTION

Use of coloured cements is quite common in construction practices, especially for architectural requirements and in finishes etc. Presently, colured cements are being produced in finished state or made at-site in the country using the following processes:

a) Addition of pigments to white cement.
b) Addition of pigments to OPC (only for dark shades).

The process of producing coloured cement by adding pigments to white cements is simple but it entails the use of white cement, the manufacture of which requires select grade raw materials and oil as fuel. Moreover, the pigments are not only costly but may also have to be imported in certain cases. White cement based coloured cements are thus expensive. Further, the quality of coloured cement obtained does not remain the same as that of the parent white cement; it gets impaired due to the addition of inert materials in the form of pigments/dyes. Also certain colours fade away under highly alkaline conditions during hydration and exposure to normal weathering conditions. This restricts the use of white portland cement based coloured cements.

Pigments can also be added to ordinary portland cement in cases where only dark shades are required, this has the advantage of lower costs.

Recently the process of obtaining coloured cements using coloured clinkers has been reported from Rumania and USSR. It is based on the introduction of ion chromophores in the clinker raw mix to produce a good colouring effect during clinkerization and cooling. Colour generation is attributed to either idiochromatism or allochromatism.

The technique offers the following advantages *vis-a-vis* process of pigment addition:

a) Utilization of lower quality raw materials compared to those used in white cement based technology.

b) Utilization of cheap and easily available ores, mine wastes, industrial wastes, etc as source of ion chromophores.
c) Improved clinker quality due to mineralizing, alloying and stabilizing effects in the presence of ion chromophores, suitable for structural purposes.
d) Uniformity and stability of colour.
e) Availability of coloured cements at comparatively low cost.
f) Partial/total elimination of high cost pigments.

TECHNOLOGICAL DEVELOPMENTS

Scope of studies conducted in USSR included basic research, establishment of process parameters and upscaling of the technology to pilot plant/semi industrial scale. So far, clinkers of yellow, green, emerald green, dark blue green, sky blue, yellow brown and black colours have been reported, wherein suitable ion chromophores like chromium, manganese, cobalt, nickel, iron and copper have been incorporated. Of these, green, greenish yellow, sandy yellow and black clinkers have been prepared using natural raw materials, industrial wastes, etc, on semi-industrial scale in the pilot plant of experimental workshop of Giprocement, wherein clinker was burnt in a rotary furnace, cooling schedule of clinkers was ascertained based upon the mineralogical composition of clinker, nature of chromophore and desired colour. However, most of the work reported in literature is patented and details are not available.

R & D WORK AT CRI

In view of the above, CRI directed its R & D work to achieve the following objectives:

a) Development of an indigenous technology for coloured clinkers,
b) Utilization of cement grade raw materials, industrial wastes and mine wastes, and
c) The possibility of utilizing coal as fuel in their manufacture.

The scope of investigations was limited to the preparation of clinkers of yellow, green and brown colours, utilizing natural raw materials, industrial and mine wastes through identification of chromophore ions, of chromophore concentration, mineralogical composition of clinkers, etc and identification and optimization of burning and cooling schedules with and without coal ash.

Experimentation and Results

Ion chromophores for green, yellow and brown clinkers were incorporated in raw mixes of suitable mineralogical composition, depending upon the nature and concentration of chromophoric ion and desired colour. Initially experiments were carried out with analytical reagents to study inter-ionic effects of colour generation and identification of parameters affecting their colour characteristics. The optimized designs under optimized burning and cooling schedules were then transferred to clinkers based on cement grade raw materials (limestone, clay, laterite bauxite, iron ore, ferrochrome slag, red mud and pyrolusite, etc) which were selected based on detailed investigations on burnability of raw mixes, physico-chemical and mineralogical characteristics of clinkers with and without coal ash absorption. Colour stability and mineralogical/micro structural features of clinkers were studied using chemical optical microscopy, XRD, SEM and reflectance measurement techniques.

It has been found that clinkers of green, brown and yellow shades can be produced under normal conditions of clinkerization at 1350°-1450°C and specially chosen burning and cooling schedules, water quenching being essential.

Mineral composition, microstructural features and free lime content of some of the typical clinker samples as obtained by chemical methods and optical microscopy and SEM are presented in Table 1 and Plates I to III. It is evident that all the clinkers are low in free lime and are well burnt with well developed alite and belite.

X-ray diffraction studies (Fig 1) have indicated presence of all major clinker phases, ie, C_3S, C_2S and C_3A.

Colour stability of the cements obtained from coloured clinkers was established based on reflectance studies. Reflectance data on various samples ie, cement obtained from clinkers, hydrated cement paste samples at the age of 3, 7 and 28 days and 6 months as also on autoclaved samples are given in Table 2. The data indicate that colour stability is fairly high both in specimens cured under normal conditions as well as those treated under hydrothermal conditions and exposed to UV radiations.

Cements were also evaluated for physical performance characteristics and the data are presented in Table 3. It is seen that the clinkers are of good quality and conform to the requirements of IS : 269-1976.

TABLE 1 MINERALOGICAL CHARACTERISTICS OF COLOURED CLINKERS

Sample No		Chromophore Added	Mineralogical Composition by Optical Microscopy (%)		
			C_3S	C_2S	Interstitial
A	Green Clinker				
	G-1	Cr^{3+}	31·8	44·8	19·6
	G-2	,,	49·0	29·1	18·1
B	Yellow Clinker				
	Y-1	Ti^{4+}	44·2	37·7	18·7
	Y-2	,,	54·4	25·6	19·8
C	Brown Clinker				
	B-1	Fe^{3+}/Mn^{2+}	60·2	23·5	13·8
	B-2	,,	45·9	30·2	19·9

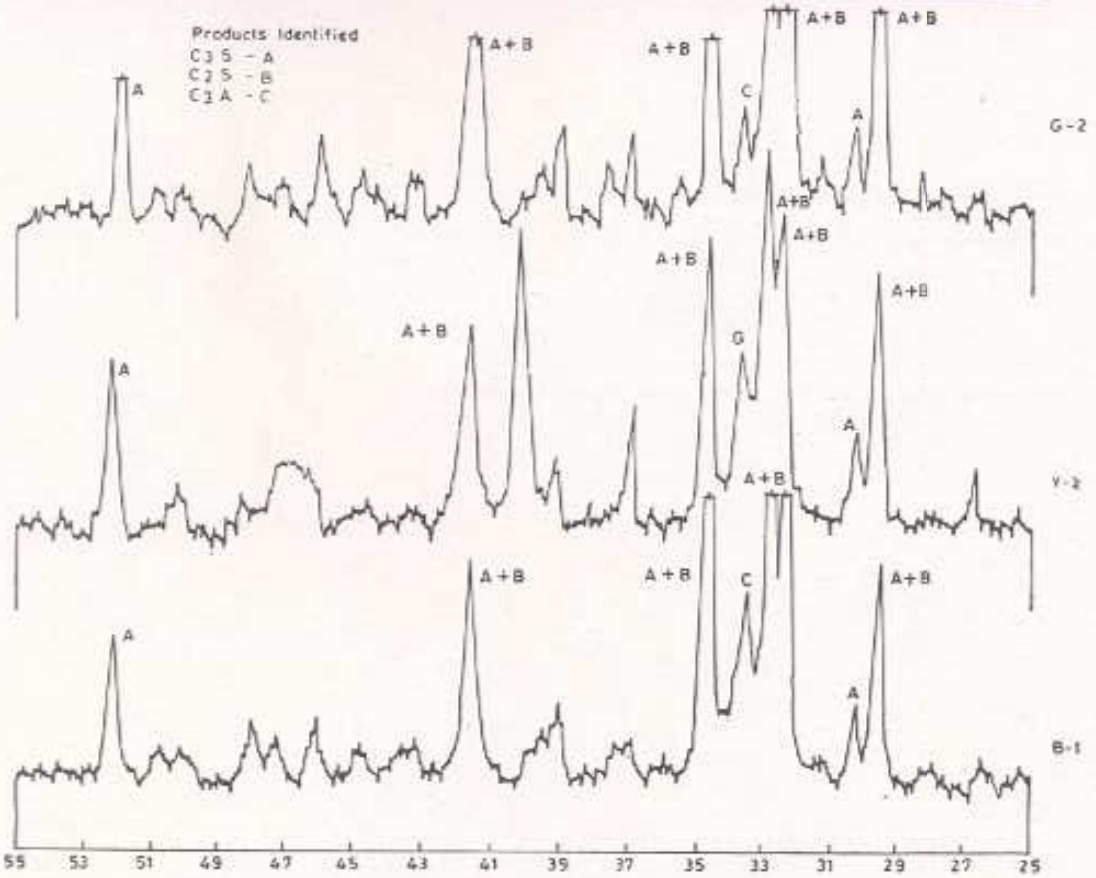

Fig 1 X-ray diffractograms of coloured clinkers

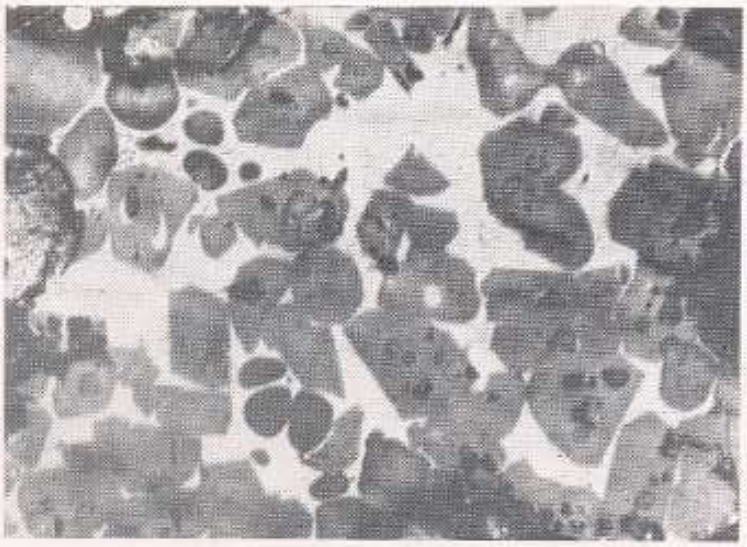

Plate I. Well developed alite and belite in green clinker

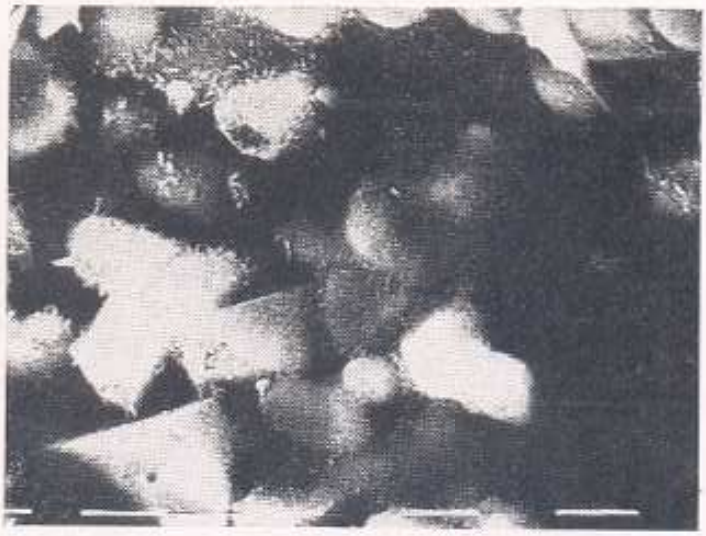

Plate II. Well developed alite and belite in yellow clinker

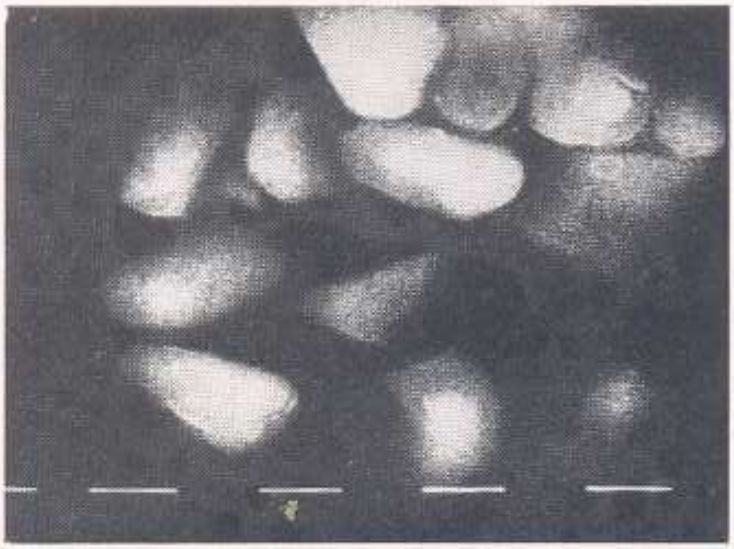

Plate III. Well developed alite and belite in brown clinker

TABLE 2 COLOUR CHARACTERISTICS OF COLOURED CLINKER

Sample No		Fineness (cm^2/g)	Wave-length ($m\mu$)	Reflectance Percent						
				Cement (Ref Sample)	Hydrated Samples				Auto-claved Sample	Sample Explosed to UV for 150 h
					3d	7d	28d	6 months		
A	Green Clinkers									
	G-1	2882	530	47·00	48·5	44	45·5	37·3	51·5	36·5
	G-2	2900	,,	50·5	42·0	43	48·0	37·3	52·5	36·0
B	Yellow Clinkers									
	Y-1	2750	570	41·0	30·28	38·27	36·26	34·5	43·0	36·0
	Y-2	2890	570	39·56	37·41	36·33	40·22	24·5	43·5	39·5
C	Brown Clinkers									
	B-1	3000	590	33·5	25·0	25·0	25·0	26·0	33·0	26·5
	B-2	2676	590	33·0	20·16	21·00	22·26	24·0	24·0	24·0

TABLE 3 PHYSICAL PERFORMANCE CHARACTERISTICS OF COLOURED CLINKERS

Sample No	Fineness (cm^2/g)	W/C Ratio	Compressive Strength (kg/cm^2) (1:3 mortar)		
			3 days	7 days	28 days
Green Clinkers					
G-1	2882	0·25	179	356	447
G-2	2900	0·25	196	344	460
Yellow Clinkers					
Y-1	2750	0·25	170	250	447
Y-2	2890	0·25	170	300	520
Brown Clinkers					
B-2	2696	0·25	250	448	590

Techno-Economics

Based on developmental work carried out so far, certain preliminary projections on the economic aspects made on comparative basis *vis-a-vis* portland cement in terms of raw material requirements, equipment and other facilities have indicated that the cost of manufacture of coloured clinker based cements will be 15-20 percent higher than that of OPC. However, it is significant to note that since the production schedule in a plant cannot be changed frequently in order to produce cement of a particular colour, the technology will be suitable for small rotary kiln based units wherein the cements of selected colours can be made based on market demand.

ASSISTANCE BY CRI

CRI will extend all the technical and technological assistance to cement plants who may wish to adopt this technology of manufacturing coloured clinkers under its technology transfer scheme.

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