

mission to publish this communication. We also wish to thank Mr. Nicasy for his skilful preparation of specimens and Mr. Beyens for the photographic work.

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¹ For a review, see the contributions by Hirsch, P. B., and Whelan, M. J., *J. Inst. Metals*, **4**, 385 (1959).

² Whelan, M. J., *Proc. Roy. Soc. A*, **249**, 114 (1958).

³ Bergezan, A., and Fourdeux, A., *C.R. Acad. Sci.*, **248**, 1333 (1959).

CHEMISTRY

Two New Complex Calcium Ferrite Phases

THE system CaO-FeO-Fe₂O₃ has been the subject of many investigations during the past decade, especially by Italian research workers studying the reduction of calcium ferrites and other ferrite phases of interest in cement chemistry. The phases CaO.FeO.Fe₂O₃ and CaO.3FeO.Fe₂O₃ have been identified by Burdese¹. No ternary phases seem to have been observed in the sub-system hematite-dicalcium ferrite-magnetite. The purpose of this communication is to report the finding of two new ternary phases in this part of the system.

In a preliminary study of the systems Fe₂O₃-CaFe₂O₄-Fe₃O₄ and CaFe₂O₄-Ca₂Fe₂O₅-Fe₃O₄ several compositions were prepared within each triangle. Varying proportions of synthetic dicalcium ferrite, hematite and magnetite powders were mixed and small pellets were pressed. These were sealed in evacuated silica capsules, which were heated at 1,000° C. for 1-10 days and then quenched in water. The pellets were examined magnetically, microscopically, by X-rays, and analysed chemically. It soon became evident that two new ternary phases exist, located one in each of the composition triangles mentioned. The two phases appear to have the following approximate compositions: 3CaO.FeO.7Fe₂O₃ located in the Fe₂O₃-CaFe₂O₄-Fe₃O₄ system and 4CaO.FeO.4Fe₂O₃ in the CaFe₂O₄-Ca₂Fe₂O₅-Fe₃O₄ system. Samples having compositions close to these formulae were non-magnetic and appeared mainly as single phases under a metallographic microscope. The stoichiometric compositions of the two new ternary phases are 24.0 per cent CaO, 7.7 per cent FeO and 68.3 per cent Fe₂O₃ for 4CaO.FeO.4Fe₂O₃ and 12.4 per cent CaO, 5.3 per cent FeO and 82.3 per cent Fe₂O₃ for 3CaO.FeO.7Fe₂O₃. Table I lists the *d*-spacings in Å. units and the relative intensities for the two phases as determined by a recording X-ray diffractometer.

The pattern of 3CaO.FeO.7Fe₂O₃ is strikingly similar to that reported^{2,3} for calcium diferrite

4CaO.FeO.4Fe ₂ O ₃		3CaO.FeO.7Fe ₂ O ₃	
<i>d</i>	<i>I/I</i> ₀	<i>d</i>	<i>I/I</i> ₀
11.3	25	15.7	20
5.6	35	5.2	10
3.74	10	4.9	25
2.99	30	3.11	20
2.81	100	2.97	40
2.67	15	2.92	15
2.52	15	2.67	40
2.49	15	2.62	35
2.29	20	2.58	100
2.24	15	2.54	30
2.06	20	2.15	20
1.84	15	1.99	15
1.73	15	1.84	15
1.58	10	1.70	20
1.50	10	1.56	20
		1.48	20

(CaO.2Fe₂O₃), suggesting that this ternary phase may be a solid solution between magnetite and calcium diferrite in analogy with other limited solid solutions in the system CaO-FeO-Fe₂O₃. Phase relationships and other data for the system hematite-magnetite-dicalcium ferrite will be reported when the current study of the oxygen potential for this system has been completed.

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Effect of High-Energy Radiation on Mixtures of Vinyl or Related Polymers with Unsaturated Compounds

A MECHANISM has been recently proposed¹ to account for the behaviour of polypropylene on irradiation, in which the formation of a cross-link between molecules involves reaction between an activated centre in the polymer and a chain fragment containing a vinylidene double bond. This suggests that the cross-linking induced by radiation would be enhanced by the incorporation of unsaturated additives into this polymer. Considerable enhancement of cross-linking has been claimed to occur in the irradiation of 'solid solutions' of polyvinyl chloride in di- and tri-allyl esters².

Consideration of the above prompted an investigation into the effect of unsaturated compounds on addition polymers in general and on polymers of the vinyl family in particular. Compounds chosen to represent three classes of unsaturation were diethyl maleate, dibutyl itaconate and triallyl cyanurate. To ensure that any enhancement would be detected, it was desirable to incorporate into the polymers as much additive as possible. However, for ease of interpretation, the concentration should lie within the range in which any reaction with the polymers could be regarded as the result of an indirect effect of the radiation on the additive. An additive concentration of 10 per cent was chosen as a reasonable compromise.

The preliminary results of this survey are presented in Table 1, the criterion for enhancement of cross-linking being the variation of sol fraction with dose for the polymer plus additive when compared with that of the polymer alone (in this table 'No' indicates

Table 1

Polymer	Enhancement of cross-linking in the presence of		
	Diethyl maleate	Dibutyl itaconate	Triallyl cyanurate
Polyethylene	None	None	Slight
Polypropylene	Slight	Slight	Good
Polyisobutylene	No	No	No
Polyvinyl alcohol	No	No	Good
Polyvinyl formal	Good	No	Good
Polyvinyl acetate	Slight	Slight	Good
Polyvinyl methyl ether	No	No	No
Polyvinyl chloride	Slight	No	Good
Polyvinyl pyrrolidone	No	No	Good
Polystyrene	No	No	Good
Polyvinyl carbazole	No	No	Good
Polymethyl acrylate	None	None	Slight
Polymethyl methacrylate	No	No	Good