

Norman F.H. B. 8/7



DEPARTMENT OF  
ENERGY, MINES AND RESOURCES  
MINES BRANCH  
OTTAWA

*A RE-EXAMINATION OF CALCIUM  
DI-FERRIC ALUMINATE IN THE  
SYSTEM CaO-IRON OXIDE- $Al_2O_3$*

A. JONGEJAN

MINERAL SCIENCES DIVISION

OCTOBER 1968



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Canada  
March 6, 1970

Dr. J. B. MacChesney  
Bell Telephone Laboratories  
Mountain Avenue  
Murray Hill, N. J.

Your ref.:- MH-1528-JBM-jh.

Dear Dr. MacChesney:

I thank you for your letter dated February 27th, enquiring concerning our work on the ternary phase occurring in the CaO-Al<sub>2</sub>O<sub>3</sub>-Fe<sub>2</sub>O<sub>3</sub> system. I am enclosing a copy of a Research Report of our work on this subject, up to the date of that report. Some crystallographic data are included but we have not done any detailed structural studies yet.

It might be of interest to you to know that Dr. R. R. Dayal, who was one of the authors of the paper you referred to, has recently joined my group as a Postdoctorate Fellow and is continuing to work in this area, with particular reference to the significance of the FeO content in the occurrence and structure of the CF<sub>2</sub>A ternary compound. It certainly has a very real effect on the type of structure formed.

Yours very truly,



Norman F. H. Bright  
Head  
Physical Chemistry Section

Encl.



555 Booth Street,  
Ottawa 1, Ontario.

February 18, 1971.

W. S. Netter, Esq.,  
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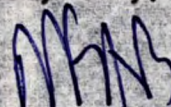
Dear Sir,

In reply to your letter dated February 1st, 1971 enquiring concerning work that we are doing on the system  $\text{CaO-Al}_2\text{O}_3\text{-Fe}_2\text{O}_3\text{-SiO}_2$  and on iron oxide reactivity, I would state that we have only published one publicly available document on the above-mentioned system, and this deals mainly with the compound  $\text{CaO} \cdot 2\text{Fe}_2\text{O}_3 \cdot \text{Al}_2\text{O}_3$ . A copy (Research Report R207) is enclosed.

Insofar as iron oxide reactivity is concerned, we have been interested in this matter for several years as part of our program on the science and technology of ferrites, in which we have been collaborating with relevant Canadian industrial organizations. In this connection, of course, the properties of the particular  $\text{Fe}_2\text{O}_3$  used are of importance. I am enclosing copies of two reports (IR 65-37 and IR 67-64) that dealing with iron oxide reactivity in this particular context.

We trust that you will find these reports of interest; there will be no charge for these documents. We thank you for your interest in our work.

Yours very truly,



Norman F. H. Bright,  
Head,  
Physical Chemistry Section.

Encls.



Mines Branch Research Report R 207

A RE-EXAMINATION OF CALCIUM DI-FERRIC ALUMINATE  
IN THE SYSTEM CaO-Iron Oxide- $\text{Al}_2\text{O}_3$

by

A. Jongejan\*

- - -

ABSTRACT

A calcium di-ferric aluminate type of compound has been prepared by several different methods. Its crystal structure appears to be very sensitive to the presence of small quantities of FeO. Since the FeO content varies during the heating and cooling of samples, it was difficult to rely on the customary quench technique to study the phase relationships in the high-iron part of the system CaO-Iron oxide- $\text{Al}_2\text{O}_3$ . An attempt has been made to determine the locations of phase-field boundaries by the use of the "cone-softening" method.

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\*Research Scientist, Physical Chemistry Section, Mineral Sciences Division, Mines Branch, Department of Energy, Mines and Resources, Ottawa, Canada.

Direction des mines  
Rapport de recherches R 207

RÉEXAMEN DE L'ALUMINATE DIFERRIQUE DE CALCIUM  
DANS LE SYSTÈME CaO-Oxyde de fer- $\text{Al}_2\text{O}_3$

par

A. Jongejan\*

RÉSUMÉ

L'auteur a préparé à l'aide de diverses méthodes un composé du type aluminat diferrique de calcium. Sa structure cristalline semble très sensible à la présence de petites quantités de FeO. Étant donné que la teneur en FeO varie au cours du chauffage et du refroidissement des échantillons, il était difficile de se fier à la technique habituelle de trempe pour étudier les relations de phase dans la zone à haute teneur en fer du système CaO-Oxyde de fer- $\text{Al}_2\text{O}_3$ . L'auteur a tenté de déterminer l'emplacement des frontières des espaces des phases en utilisant une méthode basée sur l'observation des premiers symptômes de fusion d'une éprouvette.

---

\* Chercheur scientifique, Section de la chimie physique, Division des sciences minérales, Direction des mines, ministère de l'Énergie, des Mines et des Ressources, Ottawa, Canada.

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## INTRODUCTION

Investigations in the Mineral Sciences Division, Mines Branch, of the chemical reactions taking place during the manufacture of basic refractory bricks have involved phase-equilibrium studies in parts of the multi-component system  $\text{CaO-FeO-MgO-Al}_2\text{O}_3\text{-Cr}_2\text{O}_3\text{-Fe}_2\text{O}_3\text{-SiO}_2$ . The results of some of the initial experiments, which have been reported elsewhere (1)\*, indicated that a calcium di-ferric aluminate was present in a very large region of the quaternary system  $\text{CaO-Al}_2\text{O}_3\text{-Fe}_2\text{O}_3\text{-SiO}_2$ . The possible existence of this type of compound has previously been indicated by C. Brisi (2).

The experiments were confined initially to the determination of the compatibility relations in the iron-rich part of the system  $\text{CaO-Al}_2\text{O}_3\text{-Fe}_2\text{O}_3$ . F. P. Glasser and his co-workers (3), of the University of Aberdeen, Scotland, concurrently with the latter part of our initial work, studied phase-equilibrium relationships in the same region of this system, primarily concerning themselves with the liquidus surface. An exchange of information with Prof. Glasser during their work disclosed the fact that the crystal structure of the  $\text{CF}_2\text{A}^{**}$  type of compound that had been produced at the University of Aberdeen was not the same as that produced at the Mines Branch. The publication of the results of our work on the compatibility relationships was, therefore, postponed in order to determine, if possible, the origin of the variations observed in the structure of the  $\text{CF}_2\text{A}$  type of compound.

Attempts to reproduce the  $\text{CF}_2\text{A}$  type of compound with the same crystal structure as that reported by Lister and Glasser (3) were not successful. However, the results of our experiments were consistent

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\*For references, see page 27.

\*\*NOTE: The abbreviations commonly used in literature dealing with ceramic oxides will be used throughout this report, viz., C = CaO, F =  $\text{Fe}_2\text{O}_3$ , A =  $\text{Al}_2\text{O}_3$ . Hence,  $\text{CF}_2\text{A}$  is  $\text{CaO} \cdot 2\text{Fe}_2\text{O}_3 \cdot \text{Al}_2\text{O}_3$ , or calcium di-ferric aluminate.



amongst themselves. Since these experiments had been designed with the intention of producing the  $CF_2A$  type of compound with various crystal structures, it is now considered desirable to describe the results, so that one may become aware of at least part of the problem concerning the relationship between the crystal structures and compositions of the calcium di-ferric aluminate compound.

The results of cone-softening determinations in an oxygen atmosphere in the iron-rich part of the system  $CaO-Al_2O_3-Fe_2O_3$  have been included in this report, since they were obtained by a method that consists of a direct observation of phenomena occurring at high temperatures. Results obtained by the customary quench technique were rejected early in the investigation because of the disadvantages involved in that method. In the quench technique, the composition of a sample, after quenching to room temperature, is assumed to be representative of that at the high temperature. The validity of that assumption can only be checked by the application of methods which either observe the sample directly during the heating period (e. g., hot-stage microscopy or cone-softening technique) or determine its properties at elevated temperatures (e. g., high-temperature X-ray diffraction, differential thermal and thermogravimetric techniques). Although it is possible to determine liquidus temperatures by the quench technique by discriminating between primary crystals and crystals that might have developed during the quench, not only may the composition of the phases change due to oxidation or reduction, but also the possibility exists that the liquidus temperature determined is of a low-melting or metastable form of the phases present. The possibility also existed that the crystal structure of the  $CF_2A$  type of compound might be sensitive to small variations of composition. Chessin and Turkdogan (4) had reported the compound  $CF_2$  to have this property, and it is thus not impossible that  $CF_2A$  might behave similarly.



THE INFLUENCE OF COMPOSITIONAL VARIATIONS IN THE CHEMICAL  
SUBSTANCES USED IN THE PREPARATION OF  
CALCIUM DI-FERRIC ALUMINATE

The calcium di-ferric aluminate compound has been prepared in several ways:

- (a) The composition  $\text{CaO} \cdot 2\text{Fe}_2\text{O}_3 \cdot \text{Al}_2\text{O}_3$  was prepared initially by mixing the following chemical substances in the required proportions:

$\text{CaCO}_3$  - Mallinckrodt's "Analytical Reagent" grade

$\text{Fe}_2\text{O}_3$  - Fisher Scientific's c. p. grade

$\text{Al}_2\text{O}_3$  - Baker and Adamson's reagent-grade ignited powder.

Quantities of the chemicals sufficient to yield 25-gram samples were mixed in a porcelain mortar.

The mixtures were fired for 12 hr at 1000°C in air in order to obtain a sinter by decomposing most of the calcium carbonate. The sintered mixture was then ground in an agate mortar, and pressed into 2-gram pellets. These were heated in a controlled atmosphere to a specific temperature, after which they were air-quenched.

- (b) In order to detect any possible influence of the composition of the raw materials used in the preparation on the structure of the  $\text{CF}_2^{\text{A}}$  type of compound produced, the following alternative source materials were used:

- (i)  $\text{Fe}_2\text{O}_3$  - Fisher Scientific's c. p. grade, was replaced by  $\text{Fe}_2\text{O}_3^*$  prepared by ammonia precipitation from a solution of ferric nitrate, whereby the  $\text{Fe}_2\text{O}_3$  contained only 0.01%  $\text{SO}_4$  as compared with 0.20%  $\text{SO}_4$  in Fisher's  $\text{Fe}_2\text{O}_3$ .

---

\*This  $\text{Fe}_2\text{O}_3$  was prepared by W. S. Bowman, Technical Officer, Physical Chemistry Section, Mineral Sciences Division, Mines Branch.



- (ii)  $\text{Fe}_2\text{O}_3$  - Fisher Scientific's c.p. grade was replaced by  $\text{Fe}_2\text{O}_3$  prepared by the method under "(i)", but doped with approximately 1% BaO.
- (iii) 10% (wt) of  $\text{Fe}_2\text{O}_3$  (Fisher Scientific's c.p. grade) was replaced by ferrous oxalate, of which the equivalent  $\text{Fe}_2\text{O}_3$  content was determined by weight difference after firing to  $1200^\circ\text{C}$  and cooling in an oxygen atmosphere.
- (iv) Baker and Adamson's  $\text{Al}_2\text{O}_3$  was replaced by Baker's reagent-grade aluminum hydroxide, of which the  $\text{Al}_2\text{O}_3$  content was determined from the weight loss after firing to  $1450^\circ\text{C}$ .

The products obtained using these substitutions in the firing of the mixtures at  $1300^\circ\text{C}$  in oxygen, air or  $\text{CO}_2$  atmospheres were identical with those obtained by firing the mixtures prepared according to method "a" under the same conditions. In addition, no differences were observed when the mixtures were prepared from CA, " $\text{CF}_2$ " or " $\text{AF}_2$ ", prefired at  $1200^\circ\text{C}$  in oxygen, and subsequently fired as mixtures of  $\text{CA} + 2\text{Fe}_2\text{O}_3$ , " $\text{CF}_2 + \text{Al}_2\text{O}_3$ ", or " $\text{AF}_2 + \text{CaCO}_3$ " in the various atmospheres.

The results of the foregoing experiments indicate that minor compositional variations in the raw materials used in the preparation of the  $\text{CF}_2\text{A}$  type of compound do not affect its crystal structure. One major compositional variable that was not included in the foregoing experiments was the oxygen content of the  $\text{CF}_2\text{A}$  type of compound. Consequently, the effect of the variation of the oxygen partial pressure on the preparation of the  $\text{CF}_2\text{A}$  type of compound was studied next.

THE EFFECT OF VARIATIONS OF THE OXYGEN PARTIAL PRESSURE  
ON THE PREPARATION OF THE CALCIUM DI-FERRIC  
ALUMINATE TYPE OF COMPOUND

Pellets, prepared as has been described in paragraph (a) of the previous section, were fired at 1300°C in oxygen, in air or in a CO<sub>2</sub> atmosphere. Subsolidus reactions only were involved in all preparations, since the solidus temperature of the CF<sub>2</sub>A type of compound is approximately 1435°C. The CF<sub>2</sub>A compounds that were produced appeared to have different X-ray diffraction powder patterns, depending on oxygen partial pressure. These patterns could be grouped into three principal types that could be correlated with the particular atmospheric condition maintained during the preparation of the pellets. The types of X-ray diffraction powder patterns are designated as Types 1, 2 and 3, produced respectively by pellets fired in oxygen, in air, or in a CO<sub>2</sub> atmosphere. They are listed in Table 1 (see page 7).

A Type-1 X-ray pattern, produced by a pellet fired in an oxygen atmosphere, could be changed to Type 3 by subsequently firing the pellet in a CO<sub>2</sub> atmosphere, and vice versa. Consequently, three batches of four pellets were selected, each fired in the same atmosphere and producing the same general type of X-ray diffraction powder pattern, and their FeO contents were determined\* with the following results:

The pellets that produced a Type-1 powder pattern contained 0.40%, 0.48%, 0.60% and 0.72% (wt) FeO. The pellets that produced a Type-2 powder pattern contained 0.87%, 1.84%, 1.96% and 2.35% (wt) FeO, while those producing a Type-3 powder pattern contained 3.11%, 3.83%, 6.00% and 7.48% (wt) FeO. The order in which these results are given in each

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NOTE: \*The chemical analyses were conducted by Mr. J. C. Hole,  
Analytical Chemistry Section. (See Mineral Sciences Division  
Internal Report MS-AC-68-473.)



TABLE 1

Comparison of Several Types of X-Ray Diffraction Patterns of CF<sub>2</sub>A Type of Compounds

Type 1		Type 2		Type 2a		Type 3b		Type 3		Single crystal Type C		Type 3a		Type 4a		Type 4b		Lister and Glasser (3)	
d(meas) in Å		d(meas) in Å		d(meas) in Å		d(meas) in Å		d(meas) in Å		d(calc) in Å		d(meas) in Å		d(meas) in Å		d(meas) in Å		d(meas) in Å	
I		I		I		I		I		I		I		I		I		I	
		1	10.56			1	13.57	3	13.86			4	13.36						
0.5	9.05	2	8.99	1	9.00	1	11.23	7	10.65		10.72	4	10.56						
						1	9.16	0.5	9.13					0.5	8.97				
1	8.61			1	8.60			5	8.84		8.85	4	8.79						
		4	8.54																
8	8.16	2	8.16	7	8.16													m	8.12
2	7.46			0.5	7.45														
0.5	6.44																		
6	4.88	3	4.86	6	4.88	2	4.87	0.5	6.02		4.86	5	4.85					ms	4.98
								0.5	4.89		4.81			5	4.81	4	4.82		
				0.5	4.72			0.5	4.65		4.66								
0.5	4.44	1	4.47	0.5	4.47			1	4.45		4.42								
0.5	4.22																		
							2	4.10	0.5	4.12		4.18							
3	3.69	0.5	3.70	2	3.70	1.5	3.71												
0.5	3.61	1	3.59	1	3.61			0.5	3.65		3.66								
4	3.46	1	3.45	3	3.46			4	3.52		3.57							w	3.46
								0.5	3.38		3.36	1	3.35	0.5	3.34				
2	3.28	1.5	3.26	0.5	3.27														
5	3.18	5	3.18	7	3.19			3	3.19		3.20	4	3.19	0.5	3.21			ms	3.19
								3	3.13		3.15	2	3.13	0.5	3.13			s	3.13
0.5	3.08							1	3.02		3.02								
6	2.95	4	2.95	6.5	2.96	3	2.97	1	2.98		2.96	3	2.97	8	2.96	8	2.94	m	2.96
								2	2.95		2.95								
1	2.90	4	2.89	3	2.90				2.92									w	2.90
4	2.82	2.5	2.81	5	2.82	4	2.85	7	2.84		2.88	4	2.84	0.5	2.83			w	2.81
2	2.72			2	2.72	3	2.78	7	2.77		2.76	4	2.77	0.5	2.75			w	2.71
5	2.69	3	2.69	8	2.69	8	2.67	1.5	2.68		2.68							m	2.69
1	2.65			1	2.65			1	2.66		2.66							w	2.65
		2.5	2.64					1	2.63		2.63			0.5	2.64				
								2	2.61		2.60								
											2.59								
7	2.57	10	2.56	10	2.57	1	2.58	10	2.57		2.58	10	2.56					s	2.57
7	2.54			9	2.55	8	2.53	2	2.53		2.53	2	2.53					w	2.55
3	2.51	1.5	2.51	3	2.52									10	2.52	10	2.51		
5	2.49																		
		1	2.44	6	2.45	1	2.46					1	2.44					w	2.45
						2	2.43	1	2.42										
		1	2.41	0.5	2.42	1	2.42												
								1	2.38										
3	2.35	0.5	2.35	1.5	2.36	2.5	2.34												
		0.5	2.30					1	2.31										

		0.5	2.27	1	2.27*	10	2.26*	0.5	2.28											
0.5	2.23							0.5	2.26					7	2.26*	8.5	2.25*			
3	2.20	0.5	2.20	2.5	2.20	5	2.16	0.5	2.20											
10	2.12	9	2.12	9	2.12	2	2.13	9	2.12					8	2.12					
						1	2.09									7	2.09	6	2.08	
						4	2.06	0.5	2.07											
3	2.01	0.5	2.00	2	2.00															
		0.5	1.980																	
4	1.959	0.5	1.957	2	1.957*	7	1.957*	1	1.955					5	1.954*	6	1.952*			
1	1.937	0.5	1.938	1	1.938									1	1.940					
		0.5	1.908																	
2	1.895	0.5	1.892																	
					0.5	1.851														
1	1.839				0.5	1.836														
0.5	1.778	0.5	1.778																	
		0.5	1.760					2	1.742											
0.5	1.736	0.5	1.738																	
		0.5	1.716																	
								1	1.701											
1	1.688															3	1.706	4	1.700	
0.5	1.672																			
8	1.631					7	1.632													
		8	1.626																	
								5	1.618											
		0.5	1.601																	
		0.5	1.591					1	1.595	2	1.597					7	1.606	7	1.601	
								1	1.575											
								4	1.564											
1	1.557	1	1.552	0.5	1.558															
								1	1.548											
0.5	1.522																			
9	1.504	8	1.507	6.5	1.504					2	1.538									
		1	1.500	6.5	1.496	1	1.498			7	1.507			7	1.502					
		8	1.488							7	1.440			7	1.489					
								4	1.421								7	1.475	7	1.470
								5	1.388*								2	1.381*		
																			1	1.323
																			2	1.274
																			1	1.272
																			3	1.174

Note:- \*Pt interference possible.

- Type 1 - pellet fired at 1300°C in O<sub>2</sub>, air-quenched, FeO < 0.9%.
- Type 2 - pellet fired at 1300°C in air, air-quenched, 0.9% < FeO < 2.4%.
- Type 2a - small sample fired at 1300°C in air, quenched in water.
- Type 3b - small sample fired at 1425°C in air, quenched in water.
- Type 3 - pellet fired at 1300°C in CO<sub>2</sub>, air-quenched, FeO > 2.4%.
- Type 3a - small sample, fired at 1300°C in CO<sub>2</sub>, quenched in water.
- Type 4a - small sample, fired at 1425°C in CO<sub>2</sub>, quenched in water, spinel type a = 8.35 Å.
- Type 4b - small sample, fired at 1450°C in CO<sub>2</sub>, quenched in water, spinel type a = 8.33 Å.



group is not significant. The results indicate (a) that the type of X-ray diffraction powder pattern of the  $CF_2A$  type of compound can possibly be correlated with its FeO content; (b) that the FeO content of a pellet, and consequently the  $CF_2A$  type of compound, can vary in spite of the use of an apparently consistent procedure of preparation, since there was no deliberate variation of technique within any one group; and (c) that it was apparently impossible to prepare the compound  $CF_2A$  free of FeO by the methods that had been used. Since the variations in the X-ray diffraction powder patterns might be partly caused by a distortion of the crystal structure due to the quenching procedure, and/or incompleteness of reaction, the conclusion should not be drawn that these results represent solely the variation of X-ray diffraction powder patterns of the  $CF_2A$  type of compound with variations of oxygen partial pressure along the line  $CaO \cdot [2xFeO \cdot (2-x)Fe_2O_3]$ .  $Al_2O_3$ . A discrimination could be made only between the three principal types of X-ray diffraction powder pattern of the  $CF_2A$  type of compound at this stage in the studies. The results proved, however, that variations of the FeO content of the order of 1% could not be ignored, as was done in the work of Dayal and Glasser (see Reference 3(ii), pp. 195, 200).

The part of the preparation procedure that would be most subject to an unknown or uncontrolled variation is the air quenching of the pellets. Consequently, the influence of the quenching-rate variable could be refined by the use of the conventional quench technique using milligram-size samples. Pellets had been used because results of processes occurring in a couple of grams of material would be more closely related to the chemical reactions occurring in refractory bricks than would those occurring in the very small samples normally employed in the conventional quench technique.

THE EFFECT OF ATMOSPHERE AND OF QUENCHING RATE  
ON THE PREPARATION OF THE CALCIUM DI-FERRIC  
ALUMINATE TYPE OF COMPOUND

In order to obtain information about the effects of variations in the cooling rate in various atmospheres on the crystal structure of the  $CF_2A$  compound, the customary quench technique was used, whereby small samples of the mixture were quenched in platinum envelopes in three different quench media, giving three different quenching rates, and under three different atmospheric conditions. The samples were taken from the  $CF_2A$  compound formed from substances described under (a) on page 3.

The conditions maintained during the quench experiments, and the results of the X-ray diffraction powder analyses, are given in Table 2.

The experiments listed in the first horizontal row of Table 2 demonstrated that the same type of compound was apparently produced when samples from two different types of  $CF_2A$  were quenched at different velocities under the same atmospheric conditions. The sample having a Type-1 structure was prepared by heating in an oxygen atmosphere at  $1300^\circ C$  a mixture of the required amounts of  $Al_2O_3$  and  $CF_2$ , prefired at  $1000^\circ C$  in an oxygen atmosphere. The sample having a Type-2 structure was prepared by heating the same mixture in an air atmosphere at  $1300^\circ C$ . The quenches were made into various media. The atmospheric condition was discontinued a fraction of a second before the quench was made, so that the sample passed through approximately a 2-inch-thick layer of air during the fall into the quench medium.

The experiments listed in the second row of Table 2 used the Type-3 compound that was prepared by heating at  $1300^\circ C$  in a  $CO_2$  atmosphere a mixture of the required amounts of  $Fe_2O_3$  and CA, prefired at  $1000^\circ C$  in air. The results also demonstrated that the same type of structure is apparently produced by applying various quenching rates under the same atmospheric conditions. The difference in the preparation of the original sample did not appear to have any affect.



TABLE 2

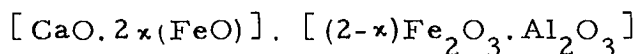
Summary of Conditions Under Which Quenches Were Made  
and Results of X-ray Diffraction Analyses of Products

Conditions of Heating	Original Sample	Medium into which Quenches were made		
		Air	Water	Mercury
Samples were heated at 1300°C in an oxygen atmosphere for 3 hr. The oxygen atmosphere was <u>not</u> maintained during the quench.	Type 1	Type 1	Type 1	Type 1
	Type 2	Type 1	Type 1	Type 1
Samples of Type 3 were heated at 1300°C for 3 hr in various atmospheres, which were <u>not</u> maintained during the quench.	Medium into which quenches were made	Atmosphere during heating period		
		Oxygen	Air	Carbon Dioxide
	Air Water Mercury	Type 1 Type 1 Type 1	Type 2 Type 2 Type 2	Type 3 Type 3 Type 3
Samples of Type 1 were heated in various atmospheres, which were <u>not</u> maintained during the quenches into water.	Temperatures (°C) from which the quenches were made	Oxygen	Air	Carbon Dioxide
	1425°C 1500°C	Type 3b Type 3b- 4 trans.	Type 3b Type 4a	Type 4b Type 4b
Samples of Type 1 were heated in various atmospheres, which <u>were</u> maintained during the quench into water.	1300°C 1450°C	Type 1 Type 3b	Type 2a Type 3b	Type 3a Type 4a

NOTE: The X-ray diffraction powder patterns of Types 1, 2, 2a, 3, 3a, 3b, 4a and 4b are listed in Table 1.

The experiments listed in the third row of Table 2 used a Type-1 compound prepared by heating at 1300°C in an oxygen atmosphere the same mixture of  $\text{Fe}_2\text{O}_3$  and CA as for the second-row experiments. The results of the experiments indicate that quenches made from 1425°C and 1500°C, i. e. from temperatures slightly below and somewhat above the solidus temperature of  $\text{CF}_2\text{A}$  (1435°C), respectively, produced variations in the X-ray diffraction powder patterns of the  $\text{CF}_2\text{A}$  products. The differences can probably be attributed to variations in the FeO content of the quenches, since more reduction of  $\text{Fe}_2\text{O}_3$  can be expected to take place at higher temperatures, even in an oxygen atmosphere.

The formation of a compound with a spinel structure can be expected when the FeO content becomes appreciable and compositions having the general formula



are produced by reduction of some of the ferric iron to ferrous.

The small difference between X-ray patterns of the two samples in the third row produced in oxygen, as compared with the larger difference between the patterns of the samples produced in air, is significant. It possibly indicates that the presence of liquid at 1500°C and not at 1425°C affects the resultant crystal structure less than does the difference in oxygen partial pressure, since the temperature difference (1425°C or slightly below, and 1500°C, well above the solidus) in an oxygen atmosphere affects the resultant crystal structure less than the same temperature difference in an air atmosphere. The field boundary of the spinel field in the system CA-FeO- $\text{Fe}_2\text{O}_3$  would thus appear to be located between 1425°C and 1500°C at the oxygen partial pressure of air.

The experiments listed in the fourth row of Table 2 used the same sample as for the third-row experiments. The results indicate that the maintenance of the atmospheric conditions during the quench was a factor in the variation in the crystal structure of the  $\text{CF}_2\text{A}$  compound, in addition to the variations produced by quenching from various temperature levels. A transformation of the crystal structure can thus take place during the extremely small time period in which a quench is made. The atmosphere in the

experiments listed in the fourth row was maintained during the quench, and this condition made the results of quenches from 1300°C differ from those listed in the other rows. The differences in the  $CF_2A$  structure obtained within the fourth-row experiments themselves are thus due to the variation in the atmosphere only. It is also significant that quenching in the same atmospheric condition (air), but from different temperatures in the sub-solidus, namely, from 1300°C in the fourth row and from 1425°C in the third row, produced different types of  $CF_2A$  structure, i. e. Type 2a from 1300°C and Type 3b from 1425°C. In these instances, the atmospheric conditions were the same throughout both experiments, since the quenching was in air.

Thermogravimetric analyses were done in the three different atmospheres to give an indication of the maximum variation encountered in the FeO content of the compounds produced under various conditions. The variations could be considered to be maximum, because of the slow rates of heating and cooling employed in thermogravimetric analyses as compared with the rapid cooling rates inherent in the quenching technique. The samples used in the thermogravimetric analyses were taken from the same mixture as that used in the three last rows of Table 2. The results of these analyses are listed in Table 3.

The percentage weight changes in Table 3 are expressed as a weight per cent of the initial sample. The information in that table indicates that the reduction and oxidation processes in the heating and cooling cycles, respectively, are not the reverse of each other and that they are complex. It will be seen, from the over-all weight losses recorded in the right-hand column of Table 3, that significant weight losses, indicating the development of considerable proportions of FeO in the samples, had occurred; further, it will be seen that they are in the same order with regard to variations of atmosphere as the chemical analytical figures reported on page 5. Since weight changes, presumably involving changes in FeO content, are observed during heating and cooling, it is reasonable to suppose that changes in crystal structure will occur in the samples at various temperatures; these, however,



TABLE 3

Results of Thermogravimetric Analyses of the Mixture  
(CA + 2Fe<sub>2</sub>O<sub>3</sub>) in Various Atmospheres\*

Atmosphere	Heating Cycle**		Cooling Cycle**		Total Weight Change (%)
	Temp. Range (°C)	Weight Change in Temp. Range (%)	Temp. Range (°C)	Weight Change in Temp. Range (%)	
Oxygen	Room temp. to 390°	-0.26	1375°-600°	-0.00	-1.09
	390°-460°	-0.32	600° to room temp.	-0.32	
	460°-1375°	-0.19			
Air	Room temp. to 510°	-0.20	1400°-1200°	+0.46	-1.22
	510°-550°	-0.26	1200°-800°	+0.26	
	550°-670°	+0.07	800° to room temp.	-0.18	
	670°-790°	-0.52			
	790°-1220°	-0.13			
	1220°-1400°	-0.72			
Carbon Dioxide	Room temp. to 315°	-0.32	1360°-1150°	+0.13	-2.26
	315°-705°	+0.26	1150°-600°	-0.26	
	785°-1000°	-0.84	600° to room temp.	+0.12	
	1000°-1160°	-0.19			
	1160°-1360°	-1.16			

\*These thermogravimetric analyses were conducted by R. H. Lake, Technical Officer, Physical Chemistry Section, Mineral Sciences Division, Mines Branch.

\*\*Heating rate: 385 deg C/hr; cooling rate: not controlled but lower than heating rate.

have not yet been studied on the thermogravimetric analysis samples, nor is it yet known at what temperatures these changes may have been arrested on cooling. This is an aspect of the whole problem that remains to be studied in the future.

The possibility is very great that some conclusions drawn from results of experiments involving indirect methods such as the quench technique would be misleading. Only direct methods, such as high-temperature X-ray diffraction procedures, could produce results that would be representative of the compositions existing at high temperatures.

#### RESULTS OF X-RAY DIFFRACTION INVESTIGATION OF SINGLE CRYSTALS OF THE CALCIUM DI-FERRIC ALUMINATE TYPE OF COMPOUND

In order to establish whether the X-ray diffraction powder patterns that were obtained in the foregoing experiments were those of one compound only in any given experiment or were produced by more than one compound, single crystals were hand-picked from quenched melts of compositions along the line  $CF_2$ - $CF_2A$ . The melts were quenched in water from temperatures at which crystals had formed on slow cooling (cooling rate, approx. 30 deg C/hr). No other specific information concerning the production of these single crystals can be given, since a factor of chance is involved in the production and growth of crystals suitable for investigation by the precession technique of X-ray diffraction analysis. Crystals were examined for homogeneity with the petrographic microscope. They appeared to be anisotropic and pleochroic from deep red or brown to yellowish-red. A total of thirty-six crystals was selected for examination by the precession technique in order to detect the presence of the various possible structures. Three different types of monoclinic structures were found among the single crystals. Two crystals, of which the cell sizes are reported here, were obtained from a crucible that contained the composition  $CF_2A$ . The other crystal was taken from a crucible containing the composition 19%  $CF_2A$ , 81%  $CF_2$ . This does not mean that the

occurrence of single crystals with these specific crystal structures was necessarily restricted to these compositions. It appeared that the contents of each crucible varied greatly from point to point. In fact, a plate-like crystal was picked out of a crucible containing the composition  $\text{CF}_2$ , that appeared to have a hexagonal structure and could possibly be considered to be the metastable iron analogue of  $\text{CA}_6$ . Its cell dimensions were  $a = 5.676 \text{ \AA}$  and  $c = 22.27 \text{ \AA}$ .

In Table 1 and in the succeeding discussion here, only the X-ray diffraction powder patterns of homogeneous mixtures having the original bulk composition  $\text{CaO} \cdot 2\text{Fe}_2\text{O}_3 \cdot \text{Al}_2\text{O}_3$  have been designated numerically as to type of structure (e.g., Type 1, etc.). The single crystals were obtained from crucibles containing heterogeneous mixtures of crystals, so that their chemical compositions were unknown. The three monoclinic single-crystal types have, therefore, been designated as "a", "b" and "c". However, when the X-ray powder diffraction patterns that could be calculated from the single-crystal data agreed with that of one of the  $\text{CF}_2\text{A}$  polymorphs, then no other inference can be drawn than that the composition of that particular single crystal was, in fact,  $\text{CF}_2\text{A}$ .

The information about the three different types of monoclinic structure determined from single crystals is given in Table 4. The crystals were considered to have their b-axes unique and perpendicular to the platy a-c plane. Types "b" and "c" differed only in the value of their b-axes. The X-ray diffraction powder pattern of Type 3, produced by firing pellets in a  $\text{CO}_2$  atmosphere (see Table 1), agrees well with that calculated from the cell parameters of the single-crystal type "c". This comparison is shown in Table 1. The formation of a  $\text{CF}_2\text{A}$  type of compound with a relatively high FeO content could be expected in the mixture in which the type "c" single crystal was found. It contained relatively more iron oxide than corresponds to the  $\text{CF}_2\text{A}$  composition and would, therefore, produce more FeO than would  $\text{CF}_2\text{A}$  itself under the same conditions.



TABLE 4

Crystallographic Information on Various Types of Structure  
of the CF<sub>2</sub>A Type of Compound\*  
(Obtained from single-crystal studies)

Crystal Structure	Crystal System	Cell Dimensions				Extinction Rules	Possible Space Group	Composition of Source Material
		a (Å)	b (Å)	c (Å)	β			
Type "a"	Monoclinic	10.32	17.95	11.99	124.55°	(hk $l$ ) all present (h0 $l$ ) only with $l=2n$ (0k0) all present	C <sub>2h</sub> <sup>4</sup> -P 2/c C <sub>s</sub> <sup>2</sup> -Pc	CF <sub>2</sub> A
Type "b"	Monoclinic	9.87	21.15	5.25	100.05°	(hk $l$ ) only with $h+k=2n$ (h0 $l$ ) only with $h=2n, l=2n$ (0k0) only with $k=2n$	C <sub>2h</sub> <sup>6</sup> -C 2/c C <sub>s</sub> <sup>4</sup> -Cc	CF <sub>2</sub> A
Type "c"	Monoclinic	9.87	21.44	5.25	100.00°	Same as for Type "b"	Same as for Type "b"	19% CF <sub>2</sub> A 81% CF <sub>2</sub>

\*This information was supplied by J. F. Rowland, Research Scientist, Crystal Structure Group, Mineral Sciences Division, Mines Branch.

It seems evident that the crystal structures occurring in the iron-rich part of the system  $\text{CaO-Al}_2\text{O}_3\text{-Fe}_2\text{O}_3$  are closely related. The similarity between X-ray diffraction powder patterns obtained in the experiments described in the previous sections and those which could be calculated from single crystals indicates that the patterns listed in Table 1 do indeed represent patterns of specific compounds and/or their polymorphs.

#### RESULTS OF CONE-SOFTENING DETERMINATIONS IN THE SYSTEM $\text{CaO-IRON OXIDE-Al}_2\text{O}_3$

Because of the evidence that only those results that were obtained by direct methods would be representative of the conditions extant at high temperatures, use has been made of the cone-softening technique (5). This method involves the direct observation of the beginning of the deformation of the shape of a small pellet on heating, which is indicative of the presence of the first traces of liquid. Discontinuities in the curves of cone-softening temperature plotted against composition are observed at phase-boundary lines. A few examples of the results of such experiments will be given and will be compared with results obtained by Dayal, Lister and Glasser (3) relating to the phase diagram of the system  $\text{CaO-Iron oxide-Al}_2\text{O}_3$ .

The X-ray diffraction powder patterns of the  $\text{CF}_2\text{A}$  type of compound that were produced by quenches of compositions that had also been subjected to cone-softening determination indicated that variations occurred that are not represented among the various types listed in Table 1. Since the patterns listed in this table refer only to materials having the bulk composition  $\text{CaO}.2\text{Fe}_2\text{O}_3.\text{Al}_2\text{O}_3$ , and since the quenches were made of materials having compositions other than  $\text{CF}_2\text{A}$ , the patterns in the latter cases were distinguished as being either of the general Type 1-2 or of the general Type 3, based upon diagnostic diffraction lines having d-spacings of  $5 \text{ \AA}$  or higher.

- (a) Mixtures having compositions along the line  $\text{CF}_2\text{A}-\text{CaO}$  were prepared. The cone-softening temperatures of these mixtures were determined in an oxygen atmosphere. Concurrently, these mixtures were also quenched in oxygen from various temperature levels and the composition of the quenches at room temperature determined by X-ray diffraction powder methods. The results of the experiments are depicted in Figure 1.

This figure and the similar subsequent figures should not be regarded as phase diagrams in the normal sense, since such diagrams give liquidus temperature data. The figures given here present two types of data: (i) the cone-softening temperatures of various compositions, indicated by open circles (O) and connected by a heavy line; and

(ii) compositions and temperatures from which the quenches were made, indicated by crosses (+). The phases shown in the various areas of these diagrams indicate the nature of the predominant phase observed in the X-ray diffraction powder patterns of the appropriate quenches. The diagrams are, in general, not subdivided by specific phase-boundary lines.

The information to be gleaned from the results in Figure 1 that is pertinent to the phase equilibria in the system  $\text{CaO}-\text{Iron oxide}-\text{Al}_2\text{O}_3$  is that the line  $\text{CaO}-\text{CF}_2\text{A}$  crosses two phase-field boundaries, at 16.5% and at 25%  $\text{CaO}$  respectively. This is shown by the discontinuities in the cone-softening curve. The results of the X-ray diffraction powder patterns of samples quenched in the solidus indicate that a join is intersected at room temperature at approximately 19%  $\text{CaO}$ .

- (b) Mixtures with compositions along the line from  $\text{CF}_2\text{A}$  to  $\text{Fe}_2\text{O}_3$  were prepared. The cone-softening temperatures of these mixtures were determined in an oxygen atmosphere. These compositions also were quenched in oxygen from various temperature levels and the composition of the quenches analysed using the X-ray diffraction powder technique. The results of the experiments are given in Figure 2.



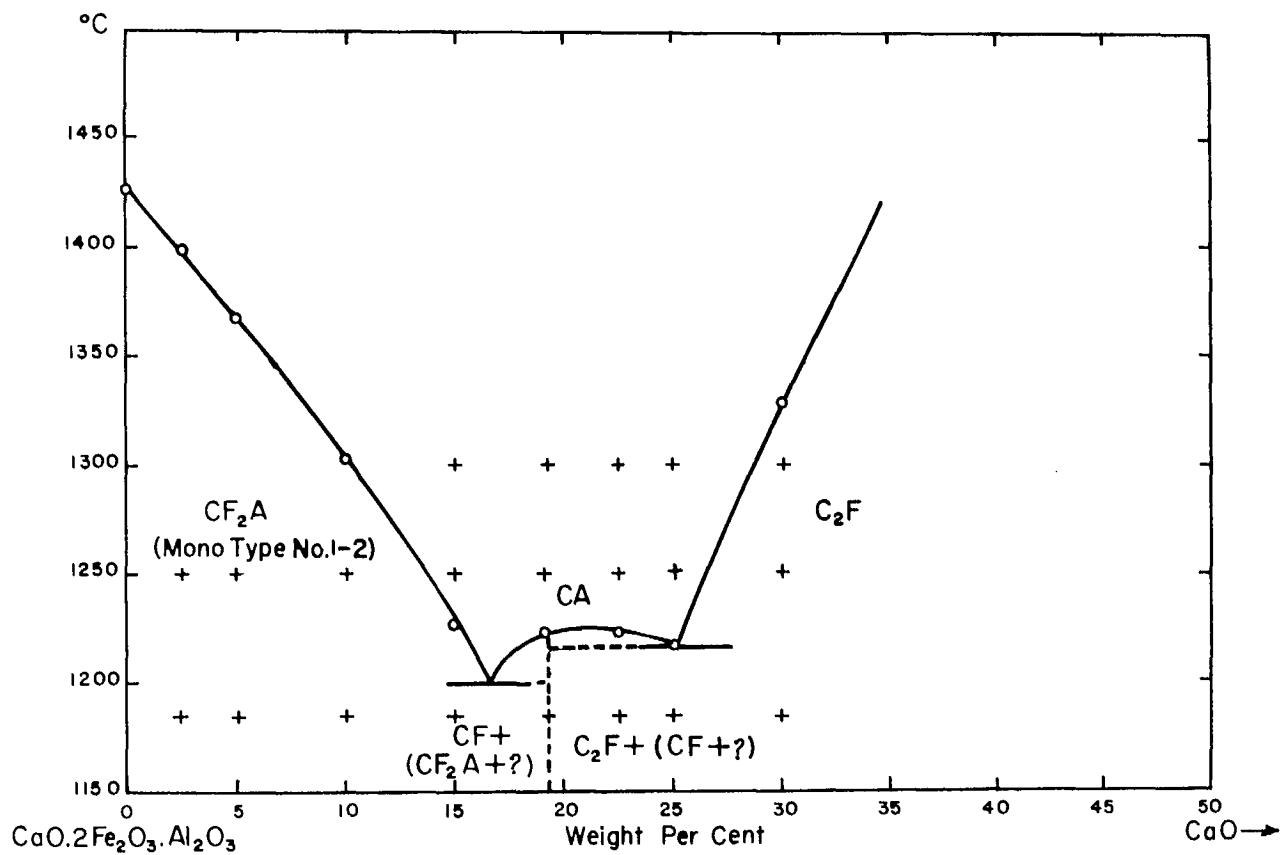


Figure 1. The cone-softening curve (O) along the line  $CF_2A$ -CaO, and the temperatures (+) from which mixtures were quenched for subsequent X-ray diffraction powder analysis.

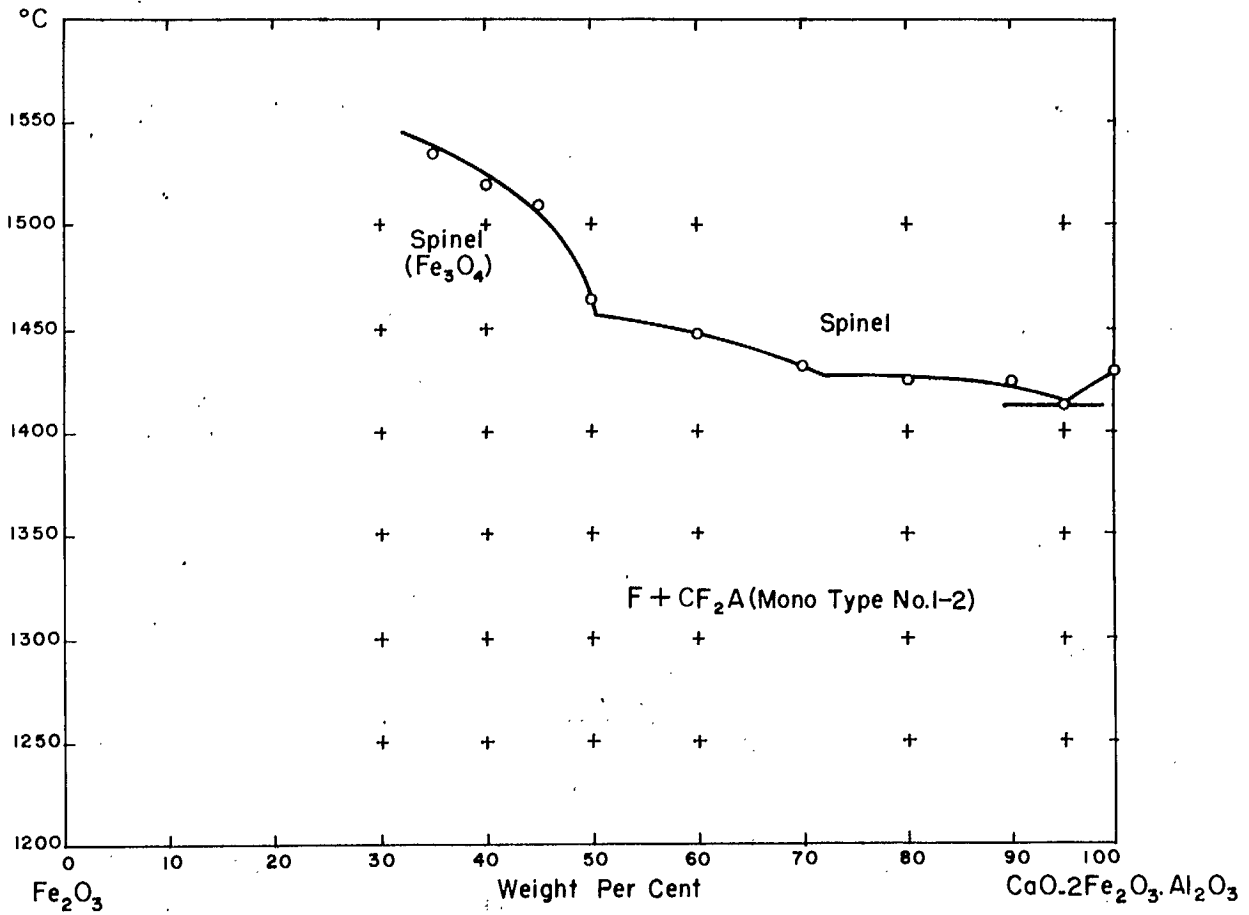


Figure 2. The cone-softening curve (O) along the line  $CF_2A-Fe_2O_3$ , and the temperatures (+) from which mixtures were quenched for subsequent X-ray diffraction powder analysis.

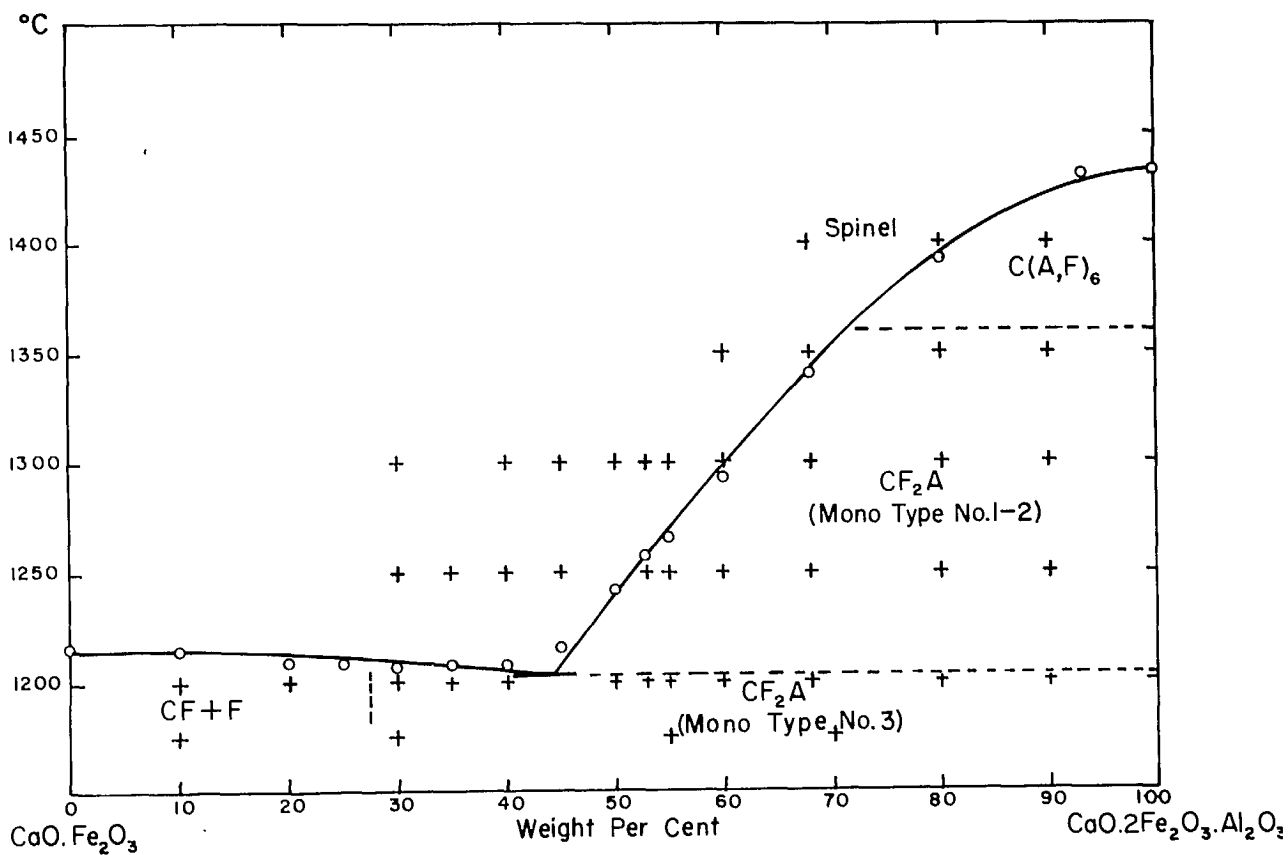


Figure 3. The cone-softening curve (O) along the line  $\text{CF}_2\text{A}$ -CF, and the temperatures (+) from which mixtures were quenched for subsequent X-ray diffraction powder analysis.

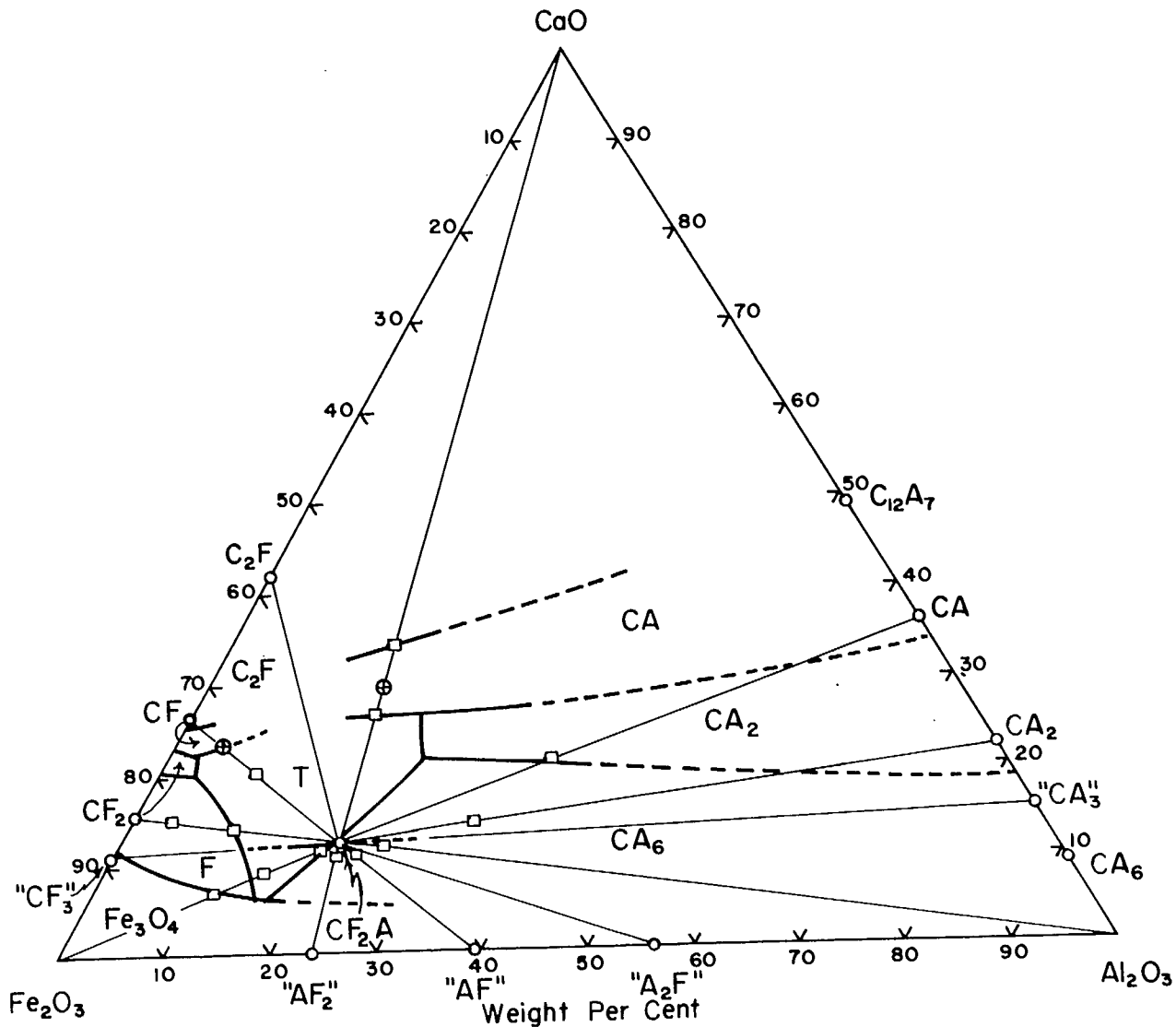
The results indicate intersection points of the line  $\text{CF}_2\text{A}-\text{Fe}_2\text{O}_3$  with at least two, and possibly three, phase-field boundaries at 49%, 72% and 95%  $\text{CF}_2\text{A}$ , respectively. The line  $\text{CF}_2\text{A}-\text{Fe}_2\text{O}_3$  itself appeared to represent a join at room temperature, since only  $\text{Fe}_2\text{O}_3$  and  $\text{CF}_2\text{A}$  could be detected in the X-ray patterns.

(c) Mixtures with compositions along the line from  $\text{CF}_2\text{A}$  to  $\text{CF}$  were also prepared. The cone-softening temperatures and the results of the X-ray diffraction analysis of quenches made from various temperature levels are given in Figure 3.

These results indicate that the presence of  $(\text{CF} + \text{Fe}_2\text{O}_3)$  in the X-ray diffraction powder patterns at room temperature is limited by a vertical line (shown broken in Figure 3) at between 20% and 30% (wt)  $\text{CF}_2\text{A}$ . The minimum temperature in the cone-softening curve, which would be indicative of an intersection with a phase-field boundary, is at approximately 45%  $\text{CF}_2\text{A}$ .

Cone-softening temperatures were also determined along parts of the lines  $\text{CF}_2\text{A}-\text{AF}_2$ ,  $\text{CF}_2\text{A}-\text{AF}$ ,  $\text{CF}_2\text{A}-\text{Al}_2\text{O}_3$ ,  $\text{CF}_2\text{A}-\text{CA}_2$ ,  $\text{CF}_2\text{A}-\text{CA}$ ,  $\text{CF}_2\text{A}-\text{CF}_2$  and  $\text{CF}_3-\text{CF}_2\text{A}-\text{CA}_3$ . Only the minima closest to  $\text{CF}_2\text{A}$  were determined along these lines. The information obtained from the results of these experiments is plotted in Figure 4, where the points of qualitative agreement and possible disagreement with the phase diagram of Lister and Glasser (see Reference 3(i), page 298) are indicated. In Figure 4, a few of the phase-field boundaries, and particularly the  $\text{CA}_2-\text{T}$  and  $\text{CA}_2-\text{CA}_6$  boundaries, have been shifted slightly in order to clarify the comparison. (The symbol "T" was used by Glasser and his co-workers to indicate the compound referred to in this report as being of the  $\text{CF}_2\text{A}$  type.) The cone-softening temperatures along the line  $\text{CF}_3-\text{CF}_2\text{A}-\text{CA}_3$  did not have any discontinuities of sufficient significance to indicate field boundaries that would be intersected according to the phase diagram of Lister and Glasser. However, the extent of the  $\text{CF}_2\text{A}$  solid solutions has been indicated along this line by heavier printing. A discontinuity in the cone-softening





**Figure 4.** Comparison between a part of the phase-equilibrium diagram constructed by Lister and Glasser (3) and the information obtained in the present studies.

Heavy lines indicate the phase boundaries of Lister and Glasser; light lines indicate the present work, except for the heavy line "CF<sub>3</sub>"-CF<sub>2</sub>A-"CA<sub>3</sub>" (see page 22, second last line).

□ - indicates minima or discontinuities in the cone-softening curves.

⊕ - indicates intersection points with joins, as established by X-ray diffraction powder analysis of quenches.

curve along the line  $\text{CF}_2\text{A}-\text{CF}_2$ , however, coincided with the field boundary between the "T" and  $\text{Fe}_2\text{O}_3$  phases of their phase diagram. This point also indicated the limit of the presence of the  $\text{CF}_2\text{A}$  type of compound in the X-ray diffraction patterns of all the quenches made on compositions along the line  $\text{CF}_2\text{A}-\text{CF}_2$ . A second discontinuity, however, did not coincide with any line in their phase diagram.

The minimum in the cone-softening curve along the line  $\text{CF}_2\text{A}-\text{CF}$  (see Figure 3) did not coincide with the field boundary between the CF and "T" phase fields in the diagram of Lister and Glasser, but the latter did coincide with the limit of the presence of our  $\text{CF}_2\text{A}$  phase in the X-ray diffraction patterns at room temperature.

Notwithstanding that the discontinuities in the cone-softening curves are indications of an unspecified nature, they are results of a method that depends upon conditions as they exist at high temperatures, and may presumably therefore be taken to refer to the high-temperature phase assemblages. It is thus very probable that, by such studies, more details could be added to the high-iron part of the phase diagram of the CaO-Iron oxide- $\text{Al}_2\text{O}_3$  system described by Glasser and his co-workers.

## CONCLUSIONS

The results of the experiments described in this report indicate the following:

- (a) The crystal structure of the  $\text{CF}_2\text{A}$  type of compound is very sensitive to its FeO content. The variation of FeO content that has been shown to affect the  $\text{CF}_2\text{A}$  crystal structure ranged from less than 0.5% (wt) to approximately 7.5% (wt). The total composition of the samples is thus difficult to convert to a simple stoichiometric formula. The type of structure variation observed is apparently similar to that observed by Chessin and Turkdogan (4) with the compound  $\text{CF}_2$ . The structure

of the  $CF_2A$  compound, however, is not sensitive to differences in composition or treatment of the oxides during its preparation.

- (b) It is possible that the structure is also sensitive to strain due to speed of quenching. This possibility is only suggested by the structure of single crystals. The powder patterns calculated from the cell dimensions of single crystals could not all be reproduced by the quench method or by firing pellets. It is more likely, however, that these operations produced differences in FeO content. The quantity of material used in each quench and that which is present in the single crystals are too small for the determinations of the FeO content by normal chemical means.
- (c) The results of thermogravimetric analyses suggest that a major cause for the occurrence of various crystal structures is associated with a combination of variations in cooling rate, and of the variation in FeO content, with the temperature from which the sample is quenched. The weight of a given sample at room temperature is not the same as that at high temperature. The cooling curve is not the reverse of the heating curve.

The consequences of the foregoing conclusions are that the most reliable method to obtain information about the phase relations in the high-iron part of the CaO-Iron oxide- $Al_2O_3$  system, and particularly those of the  $CF_2A$  type of compound, is to apply, extend and refine the methods used in the experiments referred to on page 5 and subsequently to combine the information obtained in that way with extensive thermogravimetric and differential thermal analyses. The author of this report does not claim to have provided definitive systematic information concerning phase equilibria in the high-iron part of the system CaO-Iron oxide- $Al_2O_3$  and concerning the calcium diferric aluminate type of compound in particular, but rather to have illustrated the complexities that are involved in the phase-equilibrium study of this system.

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- (c) R. H. Lake for the thermogravimetric analysis, and A. L. Wilkins for doing the quench work and for drawing the illustrations; both are Technical Officers, Physical Chemistry Section, Mineral Sciences Division.
- (d) J. C. Hole, Scientific Officer, Analytical Chemistry Section, Mineral Sciences Division, for the determination of the FeO content of various samples.



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