Constitution and Solubility of Vitreous Phosphates and Slags

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Recently various sorts of fused phosphates and slags are being used as fertilizers to supply lime, magnesia, phosphorus pentoxide, silica and other components necessary for plants. Most of these fused phosphates and slags are produced by quenching the melts with water and thus are almost vitreous containing little crystalline minerals. The constitution of such vitreous substances have not yet been clarified, though many studies have been made on crystalline minerals.

In the present work, the constitution of such vitreous substances was investigated by X-ray diffraction, and thus citrate solubility or acid solubility of those were clarified.

Experimental

Samples.—More than seventy samples including fused phosphates, slags and glasses produced in large scale or pilot plants or in the laboratory were tested by means of X-ray diffraction and microscope. Samples which were almost completely vitreous containing less than 2∼3% crystalline minerals were classified according to their chemical composition (Table I).

Samples marked as CMSP or CMASP are calcium magensium phosphate fused by electric furnaces using phosphate rock and serpentine, or by blast furnaces using phosphate rock, garnierite (nickel magnesium silicate ore) and gypsum to produce nickel matte at the same time[1,2]. Samples marked as CSP are slags of phosphorus production by electric furnaces. Samples marked as CMAFS are slags of nickel production from garnierite, limestone and gypsum. A sample CMAS-6 is a blast furnace slag of iron production.

Samples marked as CP, MP, CMP and NP were prepared by fusion of mixtures of pure chemicals in platinum crucibles. Other samples were fused in graphite crucibles in the laboratory. Each sample was fused at the temperature 100∼200°C higher than the softening point (Table I). Most of these were quenched by water and others were quenched by air.

Among these samples CMAFS-1, 2 contain 2∼3% crystalline minerals such as forstelite etc. CMAS-6 contains 2∼3% melilite (Fig. 1). Blast furnace slags containing more lime include more amount of melilite. Other samples are nearly completely vitreous, containing less than 1% crystalline materials.

Measurement of Halos by X-ray Diffractometer.—X-ray diffraction patterns of all samples were recorded by X-ray diffractometer under conditions described in Fig. 1. Every sample gave single diffraction maximum (halo) between the diffraction angle of 20∼40°. At first when recorded by the voltage of 30kV., each sample gave another maximum around 8∼15°, which diminished when the voltage was reduced to 15kV. explaining that this maximum

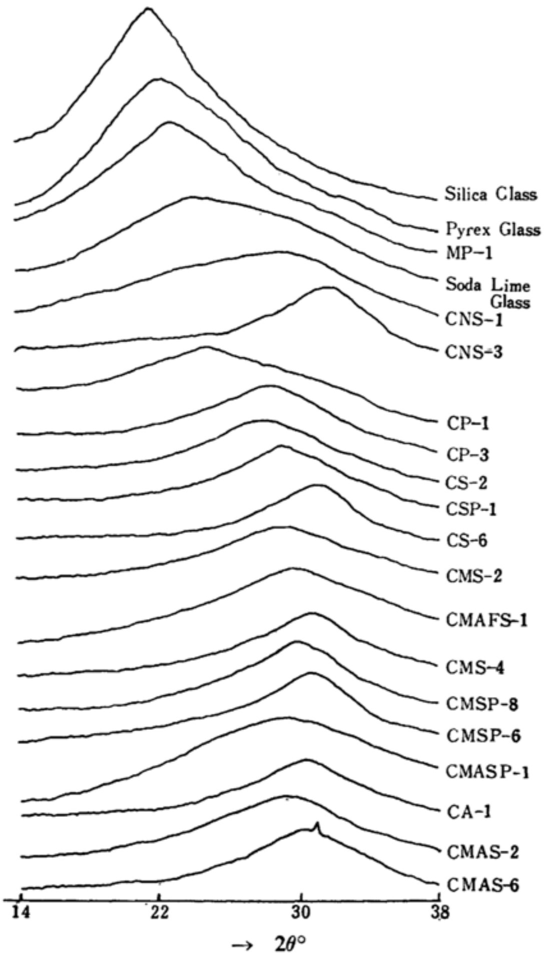

Fig. 1. X-ray diffraction patterns of samples.
Cu ray (15kV., 15 milliamp.), Ni filter
Slit 2.5°, 2.5° and 0.8 mm.
Sample area 16×33 mm.
Time constant 8 sec.
Full scale 400 counts/sec.
Scanning speed 2°/min.
Chart speed 1 cm./min.

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[1] J. Ando, *J. Chem. Soc., Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zasshi*), **61**, 1134 (1958).

[2] J. Ando, *Ind. Eng. Chem.*, **51**, 1267 (1959).

TABLE I. CHEMICAL COMPOSITION (%) AND SOFTENING POINT (°C) OF SAMPLES

Mark	SiO_2	Al_2O_3	FeO	MgO	CaO	P_2O_5	S. P.
CP-1	—	—	—	—	28.3	72.3	965
CP-2	—	—	—	—	32.7	68.0	—
CP-3	—	—	—	—	35.8	65.4	1040
MP-1	—	—	—	21.2	—	80.2	1140
MP-2	—	—	—	34.4	—	76.4	1145
CMP-1	—	—	—	14.4	17.0	68.6	990
CMP-2	—	—	—	14.4	23.2	62.2	—
CMP-3	—	—	—	24.7	19.0	56.3	1070
CMSP-1	42.1	0.7	1.4	13.7	25.8	12.6	1275
CMSP-2	40.3	1.8	0.9	15.7	26.0	12.7	1265
CMSP-3	34.0	0.8	0.8	15.7	27.8	19.0	1235
CMSP-4	39.3	0.6	1.4	16.6	26.1	12.0	1260
CMSP-5	39.0	0.6	1.6	15.7	27.4	11.8	1270
CMSP-6	26.0	2.0	1.6	18.7	30.0	19.5	1260
CMSP-7	23.8	1.3	4.1	17.1	31.0	20.6	1270
CMSP-8	21.0	2.1	0.9	10.6	38.9	25.8	1275
CMASP-1	43.0	6.0	6.5	21.7	17.0	5.7	1235
CMASP-2	29.5	7.1	3.1	11.7	30.1	18.5	1215
CMASP-3	38.0	5.3	6.1	16.8	22.9	9.3	1230
CMASP-4	32.7	5.0	6.1	15.3	28.4	13.0	1250
CASP-1	29.1	15.8	0.2	0.3	39.3	15.4	1350
CASP-2	26.5	15.1	0.2	0.4	43.5	13.6	1320
CSP-1	49.3	1.8	0.2	0.3	45.6	2.1	1425
CSP-2	46.8	1.4	0.2	0.8	49.6	1.8	1410
CS-1	65.2	0.4	—	—	34.8	—	—
CS-2	61.3	0.4	—	—	38.3	—	1430
CS-3	56.0	0.4	—	—	43.4	—	1460
CS-4	53.7	0.6	—	—	45.9	—	1490
CS-5	48.5	0.5	—	—	50.6	—	1475
CS-6	46.0	0.3	—	—	53.9	—	1440
CS-7	44.3	0.7	—	—	55.0	—	1425
CMS-1	57.8	1.0	1.2	14.0	26.0	—	—
CMS-2	55.5	0.9	0.5	12.8	29.8	—	1330
CMS-3	51.3	0.9	0.6	15.7	31.2	—	1330
CMS-4	44.6	0.6	1.0	18.8	31.9	—	1315
CMS-5	44.3	1.6	1.0	17.4	35.0	—	1380
CMAFS-1	44.7	6.6	6.6	18.0	23.6	—	1270
CMAFS-2	45.5	5.8	6.3	17.8	25.3	—	1285
CA-1	5.6	53.1	2.4	0.1	37.2	—	1420
CA-2	5.3	50.1	2.0	0.1	40.7	—	1340
CA-3	5.0	48.0	1.8	3.8	39.9	—	—
CA-4	5.8	45.2	1.5	0.2	46.2	—	1385
CAS-1	44.9	19.9	0.5	0.2	32.9	—	—
CAS-2	42.0	20.1	0.7	0.3	35.8	—	—
CAS-3	38.7	19.9	0.4	0.3	39.3	—	1270
CAS-4	36.3	20.0	0.3	0.3	41.7	—	1290
CMAS-1	45.7	13.4	0.5	6.1	32.3	—	1180
CMAS-2	42.0	14.1	0.7	6.4	34.3	—	1200
CMAS-3	38.9	15.0	0.5	6.8	36.3	—	1220
CMAS-4	35.3	15.8	0.7	7.2	38.3	—	1320
CMAS-5	32.5	15.9	1.3	9.4	38.6	—	1340
CMAS-6	32.1	16.5	0.7	7.5	40.2	—	1350
NP-1	—	(Na_2O	30.4)	—	—	69.6	—
NP-2	—	(Na_2O	36.2)	—	—	63.8	—
CNS-1	67.0	(Na_2O	17.3)	—	15.7	—	—
CNS-2	51.0	(Na_2O	25.8)	—	23.2	—	—
CNS-3	46.0	(Na_2O	33.3)	—	20.7	—	—

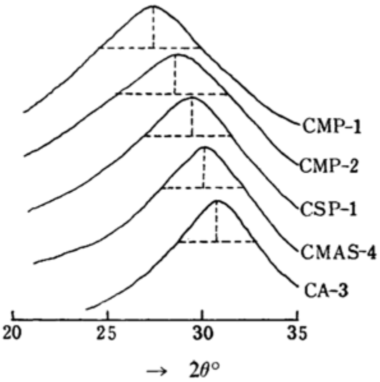

Fig. 2. Precise recording of X-ray halos and measurement of the angle of center of halos.
Cu ray (15kV. 15 milliamp.), Ni filter
Slit 2.5°, 2.5° and 0.8 mm.
Sample area 16×33 mm.
Time constant 16 sec.
Full scale 250 counts/sec.
Scanning speed 0.5°/min.
Chart speed 0.25 cm./min.

was caused by white X-ray which was not cut satisfactorily by nickel filter.

As an interesting relationship of halos to the composition of glasses was found, the halos were recorded more precisely as is illustrated in Fig. 2 in order to measure the angle of the center of halos. The diffraction angles of the center and of maximum of each halo coincide approximately but not exactly.

Measurement of Solubility.—All samples were crushed so as to have the following grain sizes: 60~100 mesh 10%, 100~200 mesh 40%, and under 200 mesh 50%. To 1 g. sample 150 ml. of 2% citric acid or N/2 (about 1.8%) hydrochloric acid was added, shaken for 5, 15, 30 or 60 min. at 20 or 30 °C, then filtered quickly using suction. The insoluble residue was dried and weighed. In this case, "Solubility" means the weight loss % measured by such method. "Solubility" when dissolved in a definite time concerns mainly the velocity of dissolution in the case of most vitreous phosphates and slags of basic composition which are dissolved completely by acids ultimately. In such case the solubility of all components of samples, lime, magnesia, alumina, silica, ferrous oxide and phosphorus pentoxide ect., are nearly the same as each other, coinciding with the solubility measured by weight loss of samples.

Some of vitreous samples containing much silica or phosphorus pentoxide are not dissolved by acids completely even when shaken for a long time but leave insoluble residue consisting mainly of a silicic or phosphoric acid component. In such cases solubility of each component was measured by chemical and X-ray analysis of the residue. Citrate solubility (at 65°C) of samples was measured similarly.

Measurement of Softening Point.—Samples were shaped into segel cones of 3 cm. height, fixed on chromite holders, and were heated at a rate of 5°C/min. Temperatures at which the cones fell were measured by platinum-platinum · rhodium thermocouple (Table I).

Results

Relationship of X-ray Diffraction Halos to Chemical Composition, Construction and Properties of Glasses.—*Outline.*—It was found that acidic samples such as silica glass, Pyrex glasses, MP-1 or MP-2 revealed a steep maximum of X-ray diffraction pattern at smaller diffraction angle of 22~24° (Fig. 1). The diffraction maximum (halo) shifts to larger angle according to the increase of the basicity of samples. Each of the samples of moderate basicity, CP-1, 2, CMP-1, soda lime glass, etc., reveals a gentle maximum around 25~29°. These samples of moderate basity have a lower softening point and are renderd to glass state most easily.

Every basic sample such as CMSP-5~8, CS-5 ~7, CA-4, CMAS-4~6, or CNS-3 reveals at larger angle of 30~32° a halo smaller than that of acidic samples but steeper than that of samples of intermediate basicity. The melts of these samples crystallize very quickly, and therefore can not be rendered to complete glass state without quenching. Samples which were more

TABLE II. RATIOS AND THEIR MEANINGS

$\mathrm{CR}=\dfrac{\mathrm{Ca}+\mathrm{Na}+(1-a)\mathrm{Al}+(1-b)\mathrm{Mg}+(1-c)\mathrm{Fe}-0.1\mathrm{P}}{1.1\mathrm{P}+\mathrm{Si}+a\mathrm{Al}+b\mathrm{Mg}+c\mathrm{Fe}}$	A ratio of the number of cations which are coordinated by six or eight oxygen ions to that coordinated by four oxygen ions.
$\mathrm{OR}_0=\dfrac{\mathrm{O}}{1.1\mathrm{P}+\mathrm{Si}+a\mathrm{Al}+b\mathrm{Mg}+c\mathrm{Fe}}$	A ratio of the number of total oxygen ions to that of cations coordinated by four oxygen ions.
$\mathrm{OR}_1=\dfrac{\mathrm{O}}{\mathrm{P}+\mathrm{Si}+a\mathrm{Al}}$	A ratio of the number of oxygen ions to that of cations the bond strength of which with oxygen is larger than 80 kcal. (Table IV).
$\mathrm{OR}_2=\dfrac{\mathrm{O}}{1.05\mathrm{P}+\mathrm{Si}+(a+0.05)\mathrm{Al}+0.5b\mathrm{Mg}}$	A part of intermediate cations was added to denominator of OR_1 (Table IV).
$\mathrm{OR}_3=\dfrac{\mathrm{O}}{1.08\mathrm{P}+\mathrm{Si}+(a+0.15)\mathrm{Al}+0.8b\mathrm{Mg}}$	Most of intermediate cations was added to denominator of OR_1.

TABLE III. EXAMPLES OF CALCULATION OF RATIOS

Samples	A.B.N.	a	b	c	CR	OR_1	OR_2	OR_3
CMP-1	—	—	0.30	—	0.40	3.17	2.90	2.76
CASP-1	44	0.50	0.08	0.05	0.96	3.14	3.05	2.92
CMAFS-2	49	0.60	0.10	0.07	1.09	3.18	3.09	3.00
CMAS-1	42	0.43	0.06	0.05	0.98	3.02	2.96	2.87
CMAS-6	52	0.71	0.12	0.07	1.23	3.23	3.12	2.97
CA-2	55	0.73	—	0.08	1.28	3.00	2.80	2.55

TABLE IV. CALCULATED BOND STRENGTH OF OXIDE COMPONENTS

M	Valence	Dissociation energy per MO_x, kcal.	Coordination number	Single bond strength B_{M-O}, kcal.	
Si	4	424	4	119	Glass formers
Al	4	402-317	4	107-79	
P	5	442	4	111-88	
Al	3	317-402	6	53-67	Intermediates
Mg	2	222	4	56	
Ca	2	257	4	66	
Mg	2	222	6	37	Glass modifiers
Ca	2	257	6	43	
Na	1	120	6	20	
Ca	2	257	8	32	

basic could not be rendered to complete glass even by rapid quenching with water.

The author thinks that halos of these glasses and vitreous substances are chiefly determined by the ratio of the number of cations coordinated by six (or eight) oxygen ions to that coordinated by four oxygen ions. This ratio is shown as "coordination ratio" (CR) in Table II and Fig. 3. X-ray is chiefly diffracted to smaller angle by oxide glasses containing much SiO_4, PO_4, MgO_4 etc. because these tetrahedra are apt to form hexagonal rings or chains having larger spacing. On the contrary, CaO_6, MgO_6, NaO_6 etc. are apt to form tetragonal rings having smaller spacing, and thus diffract X ray to larger angle. When nearly equal amount of RO_4 and RO_6 is mixed the gentle halo appears in intermediate angle.

The strongest diffraction peaks of the more basic crystalline minerals of each $CaO-P_2O_5$, $CaO-SiO_2$, $CaO-Al_2O_3$, $CaO-Al_2O_3-SiO_2$ or other systems appear usually at larger angle: e. g. $CP \rightarrow C_2P \rightarrow C_3P$, $S \rightarrow CS \rightarrow C_2S$, $C_3A_5 \rightarrow CA \rightarrow C_3A$, $CAS_2 \rightarrow C_2AS$, etc. Moreover, the diffraction angle of the strongest peak of CP (calcium metaphosphate) coincides with that of the center of the halo of the glass of the same chemical composition similarly as in the case of cristobalite and silica glass. These facts show that there is some relation between the structure of glass and that of crystalline mineral. However, the diffraction peaks of crystalline minerals and halos of glasses of the same composition do not always agree with each other.

Empirical formula indicating the relation of X-ray halo to chemical composition and constitution of glasses.—It was found that for every glasses consisting of silica, alumina, lime, phosphorus pentoxide, magnesia, sodium oxide and ferrous oxide there was simple relation between the diffraction angle (or $\lambda/\sin\theta$) of the center of each halo and the value of the above-mentioned coordination ratio (Table II, Fig. 3).

In the ratio Ca, Mg, Al, Si, etc. are the number of each ion (or atom) in a unit volume of glasses. Coefficients a, b and c are given by

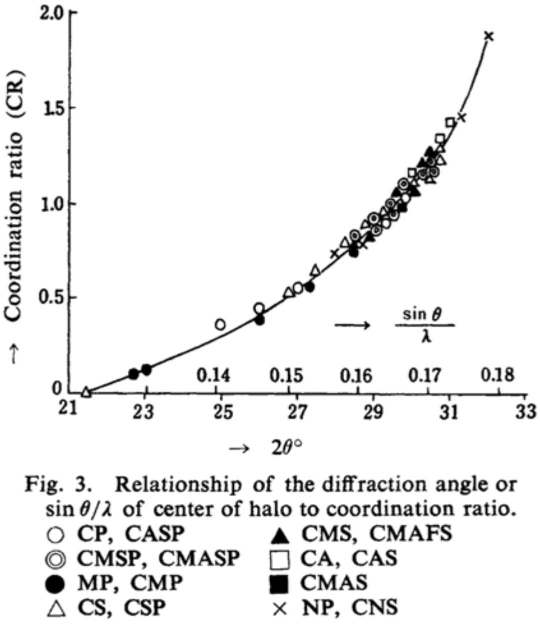

Fig. 3. Relationship of the diffraction angle or $\sin\theta/\lambda$ of center of halo to coordination ratio.

○ CP, CASP ▲ CMS, CMAFS
◎ CMSP, CMASP □ CA, CAS
● MP, CMP ■ CMAS
△ CS, CSP × NP, CNS

Fig. 4 which illustrates the relationship of the coefficients to apparent basicity number A. B. N. ($= CaO + MgO + 0.7FeO + 0.25Al_2O_3$). Here, CaO, MgO, FeO and Al_2O_3 of A. B. N. are weight % of each component of glasses. Fig. 4 was plotted empirically by trial-and-error method in consideration of both X-ray halo and solubility of glasses which will be described below. The coefficients a, b or c indicates principally a ratio of numbers of aluminum, magnesium and iron ions which are coordinated by four oxygen ions [these are described as Al(4), Mg(4) and Fe(4) below] to that of total aluminum, magnesium or iron ions respectively.

The apparent basicity number (A. B. N.) of calcium magnesium phosphate, slags of iron, nickel or phosphorus production which are being used as fertilizers is usually 47～52, and therefore, a=0.6～0.7, b=0.10～0.12, and c=0.06～0.07. In the case of aluminous glass containing much alumina the change of the coefficient a is smaller than in the case of glasses containing less alumina (Fig. 4).

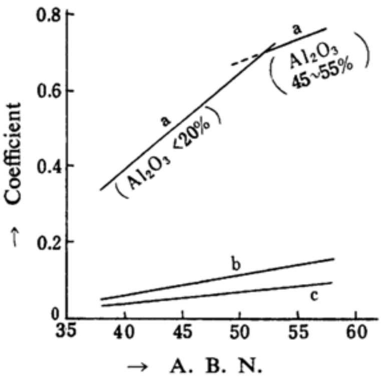

Fig. 4. Relationship of A. B. N. to the coefficients.

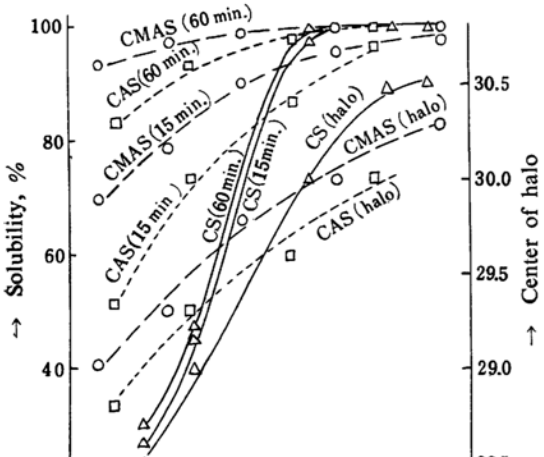

Fig. 5. Relationship of CaO/SiO_2 mole ratio to the solubility in N/2 hydrochloric acid (60 min. at 30°C) and to the angle of the center of halo.

As is illustrated by Fig. 5 both the diffraction angle of the center of each halo and hydrochloric acid solubility of samples of CS($CaO-SiO_2$) system are reduced remarkably according to the decrease of CaO/SiO_2 mole ratio. However, the reduction of both the angle and the solubility is far smaller for the samples containing a considerable amount of alumina or magnesia and alumina (samples of CAS or CMAS systems). This is attributable to the change of oxygen coordination number of aluminum and magnesium ions—much Al(4), Mg(4) and less Al(6), Mg(6) occur in basic glasses, less Al(4), Mg(4) and much Al(6), Mg(6) occur in acidic glasses as is illustrated by Fig. 4.

It was found by both X-ray and solubility tests that in glasses which contain phosphorus pentoxide more Mg(4), Al(4) and Fe(4) occurred than in silicate glasses. The amount of such four coordinated ions increases according to the amount of phosphorus pentoxide. It seems that even a part of calcium or sodium is coordinated by four oxygen ions in phosphate glasses. From this standpoint of view, coefficients of phosphorus 1.1 for denominator and −0.1 for numerator were introduced into coordination ratio (Table II) for convenience of calculation of the value of the ratio. In this way X-ray, patterns and solubilities of phosphate glasses are indicated well (Figs. 3 and 9—11).

Especilly in the case of glasses containing magnesia and much phosphorus pentoxide, an extensive amount of magnesium ions seems to be coordinated by four oxygen ions. The X-ray diffraction halos of silica glass and that of MP-1 which consists of nearly equal mole of magnesia and phosphorus pentoxide resemble each other explaining that MgP_2 plays a role of Si_3. Coefficient b to be used for calculation of coordination ratio of glasses containing more than 40% phosphorus pentoxide is given by Fig.

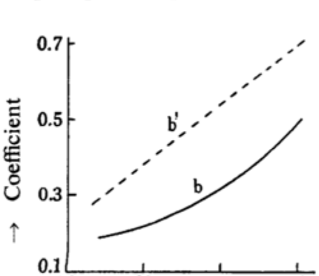

Fig. 6. Relationship of P_2O_5 content to coefficients.

6. In the case of phosphate glass the coefficient a, b or c does not indicate the ratio of the number of Al(4), Mg(4) or Fe(4) to that of total Al, Mg or Fe respectively because coefficients of phosphorus 1.1 and −0.1 are used for conveniene. The approximate ratio of the number of Mg(4) to total Mg of samples of CMP and MP systems is shown by dotted curve (b′) in Fig. 6.

Relationship of glass formation to oxygen ratio.—Oxygen ratio, a ratio of the number of total oxygen ions to that of network-forming ions, is known to relate deeply to glass formation. It was clarified by the present study that approximate oxygen ratio was calculated by ORo (Table II). Samples with the ratio less than 3.0 could easily be rendered to glass without quenching, because these are composed of long chains or networks of oxygen and network-forming ions and the melts of these are viscous. Samples with the ratio 3.0∼3.3 could be rendered to glass state completely by water quenching (CMSP-6∼8, CS-6, 7, CMS-4, 5, CA-2, 3, CMAS-5, 6, etc.). As an exception high temperature modification of calcium metasilicate (pseude wollastonite) was crystallized very quickly from the melt of the composition $CaO \cdot SiO_2$, oxygen ratio of which is 3.0. This mineral is composed of small Si_3O_9 rings³⁾ and therefore, is completely soluble in N/2 (about 1.8%) hydrochloric acid, though silicic acid component of the glass of the same composition is not dissolved by the acid.⁴⁾ Samples with the ratio larger than 3.3 could not be rendered to complete glass state even by rapid water quenching from high temperature forming crystalline minerals partly. The glass formation is affected by bond strength, too (Table IV).

Solubility of Glasses.—*Relationship of bond strength to citric and hydrochloric solubility.*—In Table IV single bond strength between oxygen and various cations⁵⁾ is illustrated. Mg(4), Ca(4) and Ca(6) were inserted by the present author into the table. Iron is thought to be intermediate between calcium and magnesium.

It was clarified in the present study that linkage Si-O, P-O or Al(4)-O, the bond strength of which is more than 80 kcal., could scarcely be broken by 2% citric acid or N/2 hydrochloric acid. The linkage Ca(6)-O, Ca(8)-O, Mg(6)-O, or Na-O, the bond strength of which is less than 50 kcal., is broken by the acids quickly. The linkage of intermediate bond strength such as Al(6)-O, Mg(4)-O, or Ca(4)-O is slowly broken by the acids.

Basic glasses containing less intermediate components are dissolved in acids very quickly

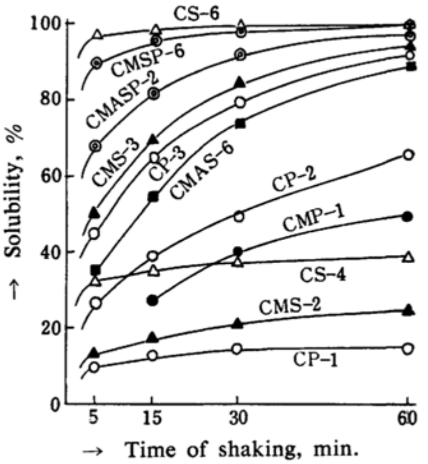

Fig. 7. Citric solubility of samples in various times at 20°C

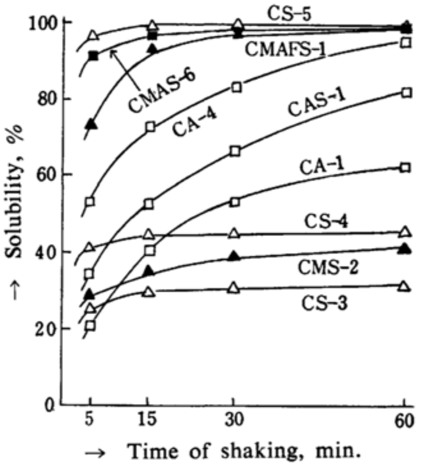

Fig. 8. Solubility of samples in N/2 HCl at 30°C.

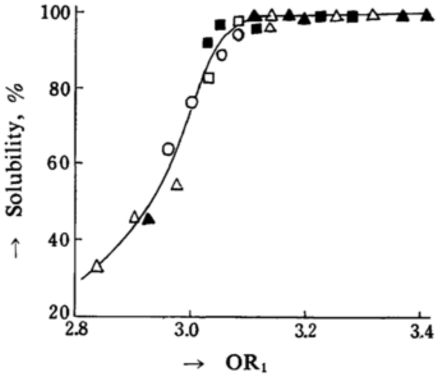

Fig. 9. Relationship of OR_1 to hydrochloric solubility in 60 min. at 30°C.
△ CS, CSP ■ CMAS
▲ CMS, CMAFS ○ CA
□ CAS

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3) J. W. Gruner, *Am. Mineral.*, 33, 681 (1948).

4) J. Ando and S. Matsuno, *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zasshi*), 62, 1481 (1959).

5) Kuan-Han Sun, *J. Am. Ceram. Soc.*, 30, 277 (1947).

(CS-6, CMSP-6 in Fig. 7, CS-5 in Fig. 8., etc.). Basic glasses containing much intermediate components dissolve slowly but completely (CMASP-2, CMS-3, CP-3, CMAS-6, CMAFS-1, CA-4, CAS-3, 4, etc.).

Acidic glasses (CP-1, CS-2, 3, 4, CMS-2, etc.) are not dissolved completely by acids but leave mainly hydrated silica or phosphoric acid component undissolved, because such glasses contain large linkage of P-O-P-O or Si-O-Si-O which forms long chains, large rings or networks. Such large linkages, the bond strength in which is larger than 80 kcal., must not be dissolved into liquid but remain as insoluble residue or as colloidal state. On the contrary, small chains or rings must enter into solution by hydration. The magnitude of the linkage is related to oxygen ratio as will be described below.

Fig. 9 illustrates the relationship of OR_1 (Table II) to the solubility of glasses when shaken in N/2 HCl for an hour at 30°C. Samples with OR_1 larger than 3.2 are dissolved completely. Samples with OR_1 smaller than 3.15 leave insoluble residue. OR_1 3.2~3.15 corresponds to $M_5O_{16} \sim M_6O_{19}$ which is the linkage of five ~six MO_4 groups and is 10~15 Å in length. It was clarified that the linkages (the bond strength in which is larger than 80 kcal.) smaller than 10 Å entered into solution and that linkages larger than 20 Å did not enter into solution usually but remained undissolved or as colloidal residue.

In citric acid the samples dissolve more slowly than in N/2 HCl. Especially the samples containing much Ca(4), Mg(4) or Al(6) are dissolved slowly and therefore not completely in an hour in 2% citric acid. It was clarified that citric solubility of samples in 60 or 15 min. at 20°C can be indicated by OR_2 or OR_3 (Table II) as is illustrated by Fig. 10 or 11.

Citric solubility of −200 mesh/inch samples is nearly equal to hydrochloric solubility of −60 mesh/inch samples treated in the same time. Hydrochloric solubility in 15 min. is nearly equal to citric solubility in 60 min. By raising the temperature from 20 to 30°C velocity of dissolution increases somewhat. Thus acid solubility of various vitreous phosphates and slags can be known from chemical composition using above relations.

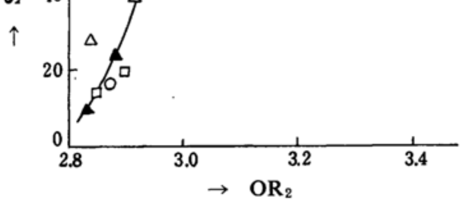

Fig. 10. Relationship of OR_2 to citric solubility in 60 min. at 20°C.

○ CP, CASP
◎ CMSP, CMASP
● CMP
△ CS, CSP
▲ CMS, CMAFS
□ CAS, CA
■ CMAS

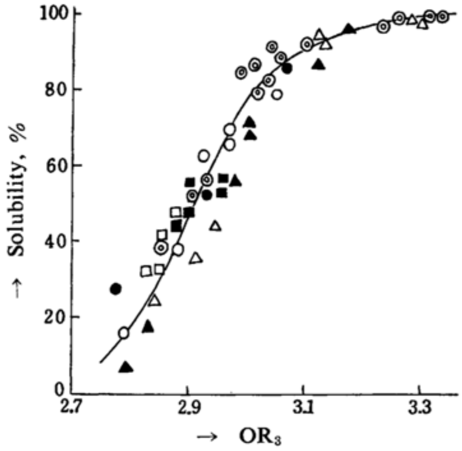

Fig. 11. Relationship OR_3 to citric solubility in 15 min. at 20°C.

○ CP, CASP
◎ CMSP, CMASP
● CMP
▲ CMS, CMAFS
△ CS, CSP
□ CAS
■ CMAS

Citrate solubility. — Citrate solubility by American official method and citric or hydrochloric solubility is quite different. For examble, CP-1 is dissolved very quickly in neutral citrate

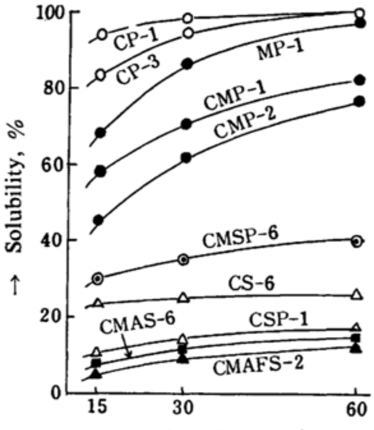

Fig. 12. Citrate solubility of samples in various times at 65°C.

though largely insoluble in acids. Phosphate glasses (CP-1—3, CMP-1—3) are dissolved more quickly in citrate but more slowly in acids when the samples are more acidic containing more phosphorus pentoxide component (Fig. 12). NH_4^+ and OH^- of the citrate must break linkages of P-O-P-O.

Silicate or aluminate glasses is dissolved slightly. Calcium magnesium phosphate, a silicophosphate glass, is dissolved intermediately in citrate (Fig. 12).

Discussion

The relation illustrated in Fig. 3 applies nearly exactly to glasses composed mainly of oxides of sodium, magnesium, aluminum, silicon, phosphorus, potassium and calcium atomic number of which is between 11 and 20. For glasses containing much boron, lithium, lead, barium etc., the atomic number of which is far smaller or far larger than that of the above elements, the relation between X-ray halo and composition of glasses is not so simple. In such cases the X-ray halo must be affected not only by coordination number of cations but also fairly intensely by ionic radius, the number of electron etc.

The above explanations of X-ray halos which was based only on coordination number and especially relations illustrated by Figs. 4 and 6 are not quite exact. However, many facts shown in the present study must be useful to clarify the construction and properties of various glasses and vitreous substances. Moreover, it is possible to determine the chemical composition of glasses by the measurement of X-ray halo.

Quenched phosphates and slags often contain small amount of crystalline minerals which affect the solubility considerably. Usually crystalline minerals dissolve far more slowly than glasses of the same composition. Crystallized forstelite, enstatite, diopside, apatite, anorthite and calcium pyrophosphate scarcely dissolve in citric acid or citrate. Gehlenite dissolves slowly, åkermanite and β-tricalcium phosphate dissolve fairly quickly in acids.[6,7] α-Calcium metasilicate[4] and α-tricalcium phosphate dissolve quickly in acids. In citrate α modification of tricalcium phosphate is highly soluble but β modification is less soluble because of the difference of velocity of dissolution which is due to the difference of structure.

Summary

The diffraction angle of center of X-ray halo of glasses composed of silica, phosphorus pentoxide, alumina, lime, magnesia, sodium oxide and ferrous oxide is principally determined by a ratio of the number of cations coordinated by six (or eight) oxygen ions to that coordinated by for oxygen ions.

Approximate ratio of the number of aluminum or magnesium ions which is coordinated by four oxygen ions to that of total aluminum or magnesium ions can be determined by measurement of X-ray halo using above relations.

Glass formation is closely related to oxygen ratio OR_0. Solubility of vitreous phosphates and slags in N/2 hydrochloric acid or 2% citric acid is indicated by the ratios OR_1, OR_2 and OR_3 all of which are calculated from chemical composition and above relations.

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6) J. Ando, *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zasshi*), **63**, 83 (1960).

7) J. Ando, ibid., **60**, 535 (1957).