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Chemical Composition and Properties of Pebble-Like Substance Precipitated during Nitric-Acidulation of Phosphate Ore

by

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A large amount of pebble-like substance, which contains fluorine in abundance, is frequently precipitated, when phosphate ores from Florida (USA) are acidulated with nitric acid containing a small quantity of sulfate ions to produce nitric phosphate solutions. TVA (USA) reported that such a water-insoluble substance was a compound called as "Chukhrovite", which consisted of fluorine, aluminium, calcium, silicon and sulfate ions[(1)].

In the present study, chemical composition and properties were investigated for the purpose of removing such impurities as fluorine, aluminium and silicon to result in purifying the nitric phosphate solution.

Phosphate Ores Used

The chemical composition of phosphate ores used is shown in Table 1.

Table.1 Chemical Composition of Phosphate Ore Used

Rock used	P_2O_5	Cao	MgO	Fe_2O_3	Al_2O_3	F	SiO_2
Florida 69	31.8	46.5	0.04	1.98	0.61	3.76	8.11
Florida 57	26.3	39.9	0.31	1.46	0.26	1.54	24.0
Florida 77	35.2	51.7	0.30	1.00	1.70	3.40	0.30
Patos de Minas 53	24.4	29.0	0.12	2.65	2.70	1.69	24.6
Jacpiranga 77	35.6	48.5	1.30	0.96	2.08	1.26	1.62
Araxá 70	32.1	40.4	0.57	5.15	5.22	2.39	3.08

Florida 69, Florida 57 and Patos de Minas 53 which are low grade sedimental ores, Florida 77 and Jacpiranga 77 which are high grade sedimental ores, and Araxá 70 which is a high grade igneous ore, were used for comparison in this study.

Formation of Chukhrovite and Its Amount

The 6 kinds of phosphate ores shown in Table 1, were acidulated respectively with 45%-nitric acid, mixed with a small quantity of additional ammonium sulfate at 80℃, and then cured for 1 to 5 hr. Precipitates obtained were filtrated to separate, washed with water and acetone, dried at 80℃, and then investigated by chemical and X-ray diffraction methods of analysis. Results from the investigation are shown in Table 2 and Fig. 1.

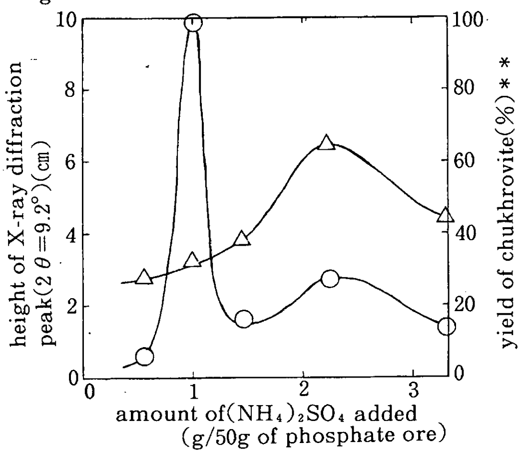

Fig.1 Yield of chukhrovite and height of X-ray diffraction peak(2θ=9.2°,cm, Cukα)*
○ : height of peak △ : yield of chukhrovite
* in the case of Florida ore(F-24〜28 in Table.2)
** calculated from the amount of fluorine precipitated

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Table.2 Formation of Chukhrovite *

Sample Mark	Phosphate ore used	Amounts of nitric acid and ammonium sulfate	Results
F-1	Florida 69 50g	45%-nitric acid 76.3ml ammonium sulfate 4.4g	no chukhrovite formed $CaSO_4 \cdot 1/2H_2O$ formed
F-2	same as in F-1	45%-nitric acid 76.3ml ammonium sulfate 2.2g	chukhrovite formed
F-11	Florida 57 50g	45%-nitric acid 76.3ml ammonium sulfate 4.4g	no chukhrovite formed $CaSO_4 \cdot 1/2H_2O$ Formed
F-12	same as in F-11	45%-nitric acid 76.3ml ammonium sulfate 2.2g	chukhrovite formed
F-21	Florida 77 50g	45%-nitric acid 76.3ml ammonium sulfate 2.2g	no chukhrovite formed $CaSO_4 \cdot 1/2H_2O$ foned slightly
F-22	same as in F-21	45%-nitric acid 76.3ml ammonium sulfate 1.45g	same as in the case of F-21
F-23	same as in F-21	45%-nitric acid 76.3ml ammonium sulfate 2.2g SiO 1.0g	same as in the case of F-21
F-24	same as in F-21	45%-nitric acid 95ml ammonium sulfate 3.3g	chukhrovite, $CaSO_4 \cdot 1/2H_2O$ and $CaSO_4 \cdot 2H_2O$ formed
F-25	same as in F-21	45%-nitric acid 95ml ammonium sulfate	same as in the case of F-24
F-26	same as in F-21	45%-nitric acid 95ml ammonium sulfate 1.45g	same as in the case of F-24
F-27	same as in F-21	45%-nitric acid 95ml ammonium sulfate 1.0g	chukhrovite and $CaSO_4 \cdot 1/2H_2O$ formed
F-28	same as in F-21	45%-nitric acid 95ml ammonium sulfate 0.55g	same as in the case of F-27
P-1	Patos de Minas 53 50g	45%-nitric acid 76.3ml ammonium sulfate 4.4g	no chukhrovite formed $CaSO_4 \cdot 1/2H_2O$ formed
P-2	same as in P-1	45%-nitric acid 76.3ml ammonium sulfate 2.2g	same as in the case of P-1
P-3	same as in P-1	45%-nitric acid 76.3ml $(NH_4)_2SiF_6$ 1.0g ammonium sulfate 2.2g	same as in the case of P-1
J-1	Jacpiranga 77 50g	45%-nitric acid 100ml ammonium sulfate 2.2g	no chukhrovite formed
J-2	same as in J-1	45%-nitric acid 100ml ammonium sulfate 1.45g	same as in the case of J-1
AR-1	Araxá 70 50g	45%-nitric acid 82ml ammonium sulfate 2.2g	same as in the case of J-1
AR-2	same as in AR-1	45%-nitric acid 82ml ammonium sulfate 1.45g	same as in the case of J-1

* Phosphate ore was acidulated with nitric acid, mixed with additional ammonium sulfate for 15 min at 80°C and then cured for 1 hr at the same temperature

It was significantly indicated that chukhrovite was easily formed in the case of using Florida ores and hardly formed in the case of using Patos de Minas, Jacpiranga and Araxá ores deposited in the central region of Brazil; even if the Florida ores were used, more amount of the additional ammonium sulfate formed more amount of semi-hydrated gypsum, resulting in less amount of chukhrovite formed.

The relationship between the amount of ammonium sulfate added and that of chukhrovite formed is shown in Fig. 1. In the figure, yield of chukhrovite was calculated from the amount of fluorine precipitated. The figure indicated that the amount of chukhrovite formed reached maximum nearly at the SO_4/F mole ratio of 1/3 or with 2.2g (theoretical amount to the fluorine content of the phosphate ore) of additional ammonium sulfate, and then decreased with decrease of the SO_4/F mole ratio; more than the theoretical amount of ammonium sulfate added formed semi- and di-hydrated gypsum in part, resulting in decrease in the amount of chukhrovite formed.

Preparation of Chukhrovite

The following A-solution was mixed with B-solution at 80℃, stirred for 30 min at the same temperature, cured for 1 day to 1 month at 30 ℃ to grow the crystals of resultant precipitates, and then filtrated to separate the precipitates. The precipitates on the filter was washed with water and acetone, dried for 1 hr at 80℃ and then investigated by X-ray powder diffraction method.

A-solution: 20g of calcium carbonate and 3.9g of aluminium hydroxide were dissolved in 200ml of 30%-nitric acid.

B-solution: 6.6g of ammonium sulfate, 7g of ammonium hydrogen fluoride and 30g of ammonium hexa-fluoro silicate were dissolved in 120ml of 28%-phosphoric acid, by using polyethylene bottle. In this case, the hydrogen fluoride and the hexa-fluoro silicate were mixed also in various weight ratio.

Results obtained are shown in Table 3. It was indicated that the formation of chukhrovite was influenced mainly by the ratio of F^- to SiF^{2-} in the B-solution; calcium fluoride was formed together with chukhrovite when the F^-/Ca^{2+} mole ratio was 7/4 (10g of ammonium hydrogen

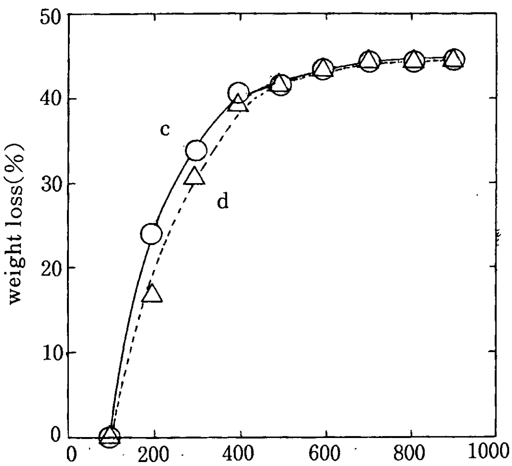

Fig.2 TG curve of chukhrovite *
the mark in the figure is the same as in Table 4
* heated for 30min at each temperature

fluoride mixed in the B-solution) or higher.

It is needed to mix both 20g or more amount of ammonium hexa-fluoro silicate(SiF_6^{2-}/Ca^{2+} mole ratio of 2.26 or higher) and 7.5g or less amount of ammonium hydrogen fluoride (F^-/Ca^{2+} mole ratio of 1.31 or lower), in order to prevent the formation of calcium fluoride, resulting in preparing chukhrovite only.

Even when no F^- was added, a small amount of chukhrovite was formed in the presence of abundant SiF_6^{2-}.

TG Test on Chukhrovite

TG test was made at 80 to 900℃ on the precipitates c and d shown in Table 3, and the result obtained is shown in Fig.2.

On heating, chukhrovite started to be decomposed at about 100℃, releasing a portion of water of crystallization; it had a considerable weight loss at 100 to 400℃ and maximum weight loss of 44.12% at about 600℃. X-ray diffraction test on the precipitates c and d heated at 900℃ indicated significantly to be mixed compounds of anhydrous gypsum $CaSO_4$, calcium fluoride CaF_2 and calcium pentafluoro aluminate $CaAlF_5$.

Chemical Composition of Chukhrovite

Chemical composition and their mole ratios of the precipitates c and d shown in Table 3 are shown in Table 4, and X-ray diffraction data are shown in Table 5.

Table.3 Effect of F^- and SiF_6^{2-} on the Formation of Chukhrovite

Sample mark	Amount of fluorine compounds mixed(g)		Mol Ratio		Curing time at 30°C(day)	Kinds of compounds precipitated
			F^-/Ca^{2+}	SiF_6^{2-}/Ca^{2+}		
a	NH_4HF_2 $(NH_4)_2SiF_6$	10 20	1.75	2.26	7	Chukhrovite CaF_2
b	NH_4HF_2 $(NH_4)_2SiF_6$	7 30	1.23	3.39	1	Chukhrovite CaF_2
c	same as above		same as above	same as above	7	Chukhrovite
d	NH_4HF_2 $(NH_4)_2SiF_6$	7.5 22.5	1.31	2.54	30	Chukhrovite
e	NH_4HF_2 $(NH_4)_2SiF_6$	0 45	0	5.08	7	Chukhrovite gelatinous silica

Table.4 Chemical Composition of Chukhrovite Prepared

Sample mark		Ca	SO_4	Al	Si	F	H_2O
c	Composition(%)	19.54	12.25	3.32	3.30	31.47	30.12*
	Mole ratio	3.97	1.04	1.00	0.96	13.5	13.6
d	Composition(%)	19.63	12.16	3.460	3.37	30.57	30.81*
	Mole ratio	3.83	0.99	1.00	0.94	12.6	13.4

* Calculated by reducing total amount of Ca, SO_4, Al, Si, F and H_2O from 100

Table.5 X-Ray Diffraction Date of Chukhrovite (CuK α)*

2θ (°)	I/I_{100}	2θ (°)	I/I_{100}	2θ (°)	I/I_{100}
9.2	100	26.1	3	35.1	8
15.0	30	27.7	8	37.4	2
17.6	6	30.2	4	38.4	3
21.3	5	31.7	4	40.4	5
23.2	6	33.9	4	41.5	16

* Sample c in Table 4

It had been already reported that the chemical formula of chukhrovite is $Ca_4SO_4AlF_6SiF_6(OH) \cdot 12H_2O$[1]. A.W.Fraxier also had reported the formula to be $Ca_4SO_4AlSiF_{13} \cdot 10H_2O$, by analyzing chemically the precipitates obtained by washing sufficiently the solids in various kinds of wet-process phosphoric acids to dissolve all of gypsum in them[2].

In the present study, it was found to be able to prepare chukhrovite easily in bench-scale test (Table 3) and to be given as $Ca_4AlSiF_{13}SO_4 \cdot (13 \sim 14)H_2O$ in chemical formula (Table 4). As described above, TG test indicated that thermal decomposition reaction of chukhrovite was given in the following equation.

$$Ca_4AlSiF_{13}SO_4 \cdot nH_2O \longrightarrow CaSO_4 + 2CaF_2 + CaAlF_5 + SiF_4\uparrow + nH_2O\uparrow$$

In this case, the value of n or molecule numbers of water of crystallization was calculated in the following way, by using the weight loss of 44.12% at 600℃.

$$(18.02n + 104.09)/(18.02n + 558.43) = 0.4412$$
$$10.07n = 142.29$$
$$n = 14.13$$

The result obtained indicated the chemical formula of chukhrovite to be $Ca_4AlSiF_{13}SO_4 \cdot 14H_2O$

Summary

A large quantity of pebble-like substance is frequently precipitated as one of by-products, when phosphate ore is acidulated with nitric acid to produce nitric phosphate solution. Study was made to clarify the chemical formula and properties of the precipitates, resulting in summarizing as described below.

(1) The pebble-like water-insoluble substance, which was formed on acidulating phosphate ore with nitric acid containing a small amount of sulfate ions, was found to be chukhrovite whose chemical formula was $Ca_4AlSiF_{13}SO_4 \cdot 14H_2O$.

(2) Chukhrovite was easily formed by mixing the phosphoric acid containing sulfate, fluoride and hexa-fluoro silicate ions with nitric acid containing calcium and aluminium ions at 80℃. In this case, maximum yield of chukhrovite was obtained at the SO_4^{2-}/Ca^{2+} mole ratio of about 0.25; higher mole ratio than 0.25 formed gypsum and lower ratio than that formed calcium fluoride, respectively in part.

(3) The formation of chukhrovite depended also upon the amount of fluoride and hexa-fluoro silicate ions; calcium fluoride was partially formed when the F^-/Ca^{2+} mole ratio was higher than 1.75. The mole ratios of F^-/Ca^{2+} and SiF_6^{2-}/Ca^{2+} are desired to be about 1.31 and 2.26, respectively, in order to form chukhrovite without precipitation of calcium fluoride.

(4) Chukhrovite was easily formed on nitric acidulation of Florida phosphate ore; maximum amount of that was obtained when sulfate ions were added at the SO_4/F mole ratio of 1/13 or the theoretical amount. In

the case of using Brazilian ores, neither sedimental one nor igneous one formed chukhrovite.

(5) On heating chukhrovite, it started to be decomposed at 100℃, and about 44% weight loss was obtained at 600℃, indicating the following reaction.

$$Ca_4AlSiF_{13}SO_4 \cdot 14H_2O \longrightarrow CaSO_4 + 2CaF_2 + CaAlF_5 + SiF_4 + 14H_2O$$

Literatures Cited

1) TVA: "Crystallographic Properties of Fertilizer Compounds, Chem Eng. Bull., No.6, p.30(1967)

2) A.W.Frazier, J.R.Lehr and E.F.Dillard: TVA Bull., No.V-113(1977)

Abstract

A large amount of pebble-like substance which contains fluorine in abundance is frequently precipitated on acidulating Florida Phosphate ores with nitric acid in the presence of a small quantity of additional sulfate to produce nitric phosphate solution.

In the present study, the water-insoluble substance was found to be easily prepared by mixing Ca^{2+} - and Al^{3+} - containing nitric solution with F^- - , $SiF_6{}^{2-}$ - and $SO_4{}^{2-}$ - containing phosphoric solution at about 80℃, and then it was determined by chemical and X-ray diffraction methods of analysis to be chukhrovite, whose chemical formula was $Ca_4AlSiF_{13}SO_4 \cdot 14H_2O$..

The formation of chukhrovite was influenced by the mole ratios of $SO_4{}^{2-}/Ca^{2+}$, F^-/Ca^{2+} and $SiF_6{}^{2-}/Ca^{2+}$; maximum yield of it was obtained at the ratios of $SO_4{}^{2-}/Ca^{2+}$ of 0.25, F^-/Ca^{2+} of about 1.31 and $SiF_6{}^{2-}/Ca^{2+}$ of about 2.26, respectively.

On heating chukhrovite, it started to be decomposed at 100℃, and about 44% weight loss was obtained at 600℃, indicating the following reaction.

$$Ca_4AlSiF_{13}SO_4 \cdot 14H_2O \longrightarrow CaSO_4 + 2CaF_2 + CaAlF_5 + SiF_4 + 14H_2O$$

フロリダリン鉱石に少量の硫酸塩を添加して硝酸で処理し，硝リン酸液をつくる際にはフッ素を多く含む小石状物質が多量に生成する．今回の研究で，この非水溶性物質が Ca^{2+} および Al^{3+} を含む硝酸溶液と F^-，$SiF_6{}^{2-}$ および $SO_4{}^{2-}$ を含むリン酸溶液とを80℃付近で混合すると容易に生成することが見出され，化学分析とX線回折によって化学式が $Ca_4AlSiF_{13}SO_4 \cdot 14H_2O$ のチュクロバイトと決定された．チュクロバイトの生成はモル比 $SO_4{}^{2-}/Ca^{2+}$，F^-/Ca^{2+} および $SiF_6{}^{2-}/Ca^{2+}$ に影響され、その最大収量はモル比 $SO_4{}^{2-}/Ca^{2+}$ 0.25，F^-/Ca^{2+} 約1.31、$SiF_6{}^{2-}/Ca^{2+}$ 約2.26で得られた．チュクロバイトを加熱すると，100℃で分解を始め、600℃で約44%の重量が減少し，次の分解反応が生じることを示した．

$$Ca_4AlSiF_{13}SO_4 \cdot 14H_2O \longrightarrow CaSO_4 + 2CaF_2 + CaAlF_5 + SiF_4 + 14H_2O$$