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RELATIONSHIP BETWEEN THE REACTIVITY AND SOME PHYSICO-CHEMICAL PROPERTIES OF ROCK-PHOSPHATE

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The steadily growing worldwide production of fertilisers has brought about an ever increasing consumption of raw materials, among which rock phosphates play the principal role. In those countries, which do not have their own sources of phosphate rock, the recent upward trends in demand as well as prices have forced many fertiliser producers to process various types of rock phosphates available on the world market at the moment. This often results in the occurrence of technological troubles connected with the change from one type of phosphate rock to a different one. Consequently, it becomes necessary to study the main characteristics of rock phosphates and to elucidate the relationships among their physical and chemical properties on the one side and their "workability" by various conventional or newly developed processes on the other side. One of the essential criteria for the treatment of rock phosphates is their reactivity, which, more or less, may be considered to be a measure of their ability to be decomposed by a mineral acid. This property affects fundamentally the performance of any decomposition equipment and, in particular, the decomposition efficiency, which can be attained economically with different technological processes. A better knowledge of the relationships between the physico-chemical characteristics of a raw material and its reactivity is very useful in evaluating and taking decisions upon the workability of rock-phosphates from various deposits, especially in the case of newly developed and exploited localities.

So far relatively few published papers have been devoted to the subject under discussion and some of these will be mentioned briefly in the following paragraphs.

JANIKOWSKI et al, (1) studied the correlation between mean particle size and surface area of various rock phosphates to the reactivity during their decomposition by sulphuric acid. The authors prove that the principal factor influencing reactivity is the external surface area. An important conclusion of this paper is a definition of the correlation between the initial surface area and the reaction time at constant temperature and sulphuric acid concentration. On the basis of this correlation and a known particle size distribution of a phosphate, the time dependence of the degree of decomposition can be assessed for a given phosphate rock and thus the method can be used for comparing the reactivity of different ore samples.

The influence of specific surface on the reactivity has been confirmed
also by CARO et al. (2). When analyzing the observations, the same
author (3) concludes that the decisive factor affecting the reactivity
of phosphates is the structure of their pores, and the key importance is
to be attributed to that portion of pores, whose radius is smaller
than 600 Å. In the study of the effects of calcination (4), the author
found an increase in the reactivity of a Utah phosphate in samples
calcined at 800-900°C; the reason for this phenomenon, however, has not
been explained. The correlation between reactivity and specific surface
was ascertained also by VEIDERMA (5) who studied various types of Soviet
apatites and phosphorites.

Important fundamental information on the subject can be found in the
papers by LEHR and his co-workers (6, 7), who have demonstrated the
relationship between the time needed for a complete decomposition by
dilute nitric acid and the crystallite size of a phosphate. These
solubility studies were carried out with a great number of phosphate
rock samples. The relation between the temperature of calcination of
rock phosphates and their solubility in a neutral ammonium citrate
solution has also been described; the solubility decreases as the calci-
nation temperature increases. The citrate solubility decreases also with
the increasing length of the a -axis of the elementary cell of the apatite
structure in phosphates.

According to NOGUCHI (8), a higher CaO/P_2O_5 ratio, a larger specific
area and a lower R_2O_3 content bring about a higher reaction rate of a
rock phosphate with sulphuric acid. ANDO and MATSUNO (9, 10) studied
the course of the acidulation of various rock phosphates with hydrochloric
and nitric acid and mixtures of phosphoric and sulphuric acid. They
found that the reactivity value always follows the order of the crystallite
size and confirmed also LEHR's conclusions concerning a drop in reactivity
of all phosphates resulting from their calcination, irrespective of the
kind of mineral acid used for the decomposition. A remarkable decrease
in reactivity was exhibited by phosphates calcined at temperatures higher
than 900°C.

Extensive investigations of rock phosphates characteristics are carried
out at the Levington Research Station (Fisons, Ltd.) and some of the
results have been published (11).

This very brief survey of the present state of knowledge of the subject
under discussion shows that the relationships between reactivity and
physico-chemical characteristics of rock-phosphates have not yet been
clarified and described adequately. Czechoslovakia belongs to those
countries which have to process exclusively imported phosphates from
various sources and of widely differring properties. The difficulties
arising from this situation have stimulated efforts devoted to studying
the discussed problems in the Research Institute of Inorganic Chemistry.

Experimental

The properties and reactivity values of rock phosphates were studied
using 9 characteristic types of phosphorites and apatites; besides also
numerous different samples as obtained from the same deposits were
tested. Three particle size fractions prepared from one phosphate
sample were examined in some cases. These fractions were : + 0.16 mm
(corresponding roughly to 100 mesh screen oversizes), - 0.16 + 0.1 mm
(- 100 + 150 mesh) and - 0.1 mm (i.e. 150 mesh screen undersizes). The
composition of the individual rock phosphates is given in Table 1.

<u>Table 1</u>

<u>Chemical composition of the rock phosphates studied</u>
(- 0.16 + 0.1 mm fraction)

Phosphate	P_2O_5 (%)	CO_2 (%)	F (%)	SiO_2 (%)	Fe_2O_3 (%)	Al_2O_3 (%)	CaO (%)
A	32.8	4.35	3.78	2.42	0.25	0.13	51.1
B	34.0	3.25	4.53	0.30	0.32	0.32	56.0
C	29.3	5.64	3.61	1.10	0.32	0.42	48.0
D	28.3	5.06	2.93	8.30	1.23	0.42	45.7
E	32.7	5.35	3.49	1.52	0.19	0.35	52.6
F	34.2	0.90	4.24	0.69	0.20	0.41	56.0
G	35.3	2.85	3.74	1.25	0.45	0.56	51.0
H	32.6	2.38	3.60	0.55	1.02	0.81	48.2
I	39.8	0.15	3.34	0.78	0.42	0.49	54.3

The table shows clearly the diversity among the individual phosphates.
E.g. the P_2O_5 content varies from almost 40% (phosphate I) to 28%
(phosphate D). Moreover, even the chemical composition of each sample
changes according to the particle size. The P_2O_5 content is generally
lower in the finer fractions. In the phosphate C the P_2O_5 content is
30, 29.3 and 26.4% in the coarse, medium and fine fractions, resp.

The phosphates studied exhibit also marked differences in their CO_2
content. This content is very high (4-6.5%) in non-calcined sedimentary
phosphorites (samples A, C, D, E), while the other phosphates contain
much less CO_2, its content being almost negligible in phosphate I
(an igneous apatite). The fluorine content is almost the same in all
the phosphates studied (3-4%).

It was necessary to remove from the phosphate samples freely tied carbonate minerals prior to some measurements. This was effected by extracting the phosphate samples by the Silverman solution (7). The CO_2 content in such treated phosphates are given in Table 2.

Table 2

CO_2 content in rock phosphates (fraction -0.16 + 0.1 mm) after extraction by Silverman solution

Phosphate	A	B	C	D	E	F	G	H	I
% CO_2	4.03	1.42	4.87	4.27	4.41	0.81	2.61	2.11	0.09

The necessary values of interplanar d spacings were determined accurately by X-ray diffraction method and from these values the lattice constants a and c of the studied rock phosphates were calculated (Table 3).

Table 3

Lattice constants a and c and half-maximum breadths of diffraction line (123) of rock phosphates

Phosphate	a ($\overset{\circ}{A}$)	c ($\overset{\circ}{A}$)	B ½ (cm)
A	9.336 ± 0.003	6.896 ± 0.001	17.2
B	9.372 ± 0.003	6.894 ± 0.002	12.8
C	9.323 ± 0.003	6.895 ± 0.003	18.4
D	9.338 ± 0.002	6.896 ± 0.001	18.6
E	9.337 ± 0.003	6.897 ± 0.001	17.0
F	9.372 ± 0.004	6.892 ± 0.002	12.0
G	9.352 ± 0.002	6.894 ± 0.003	15.2
H	9.335 ± 0.002	6.896 ± 0.001	17.2
I	9.390 ± 0.006	6.902 ± 0.004	10.6

It follows from the calculated values of the lattice constants that there does not exist a substantial difference among the c values for the individual phosphates and these results correspond to those published by other authors (10, 12, 13). The c lattice constants vary within a fairly narrow range (6.892-6.897 Å), the only exception being phosphate I (6.902 Å). Markedly larger differences occur in the values of constant a (9.323-9.390 Å), which, too, agrees with literature data.

The size of primary crystalline grains was determined by measuring the half-maximum breadth ($B_{1/2}$) of the diffraction line (123) for the rock phosphates studied. The results are also given in Table 3.

Furthermore, the infra-red absorption spectra of all the phosphates tested were measured. A characteristic intensive absorption was observed in the region around 575 cm^{-1}. Unlike the $Ca_3(PO_4)_2$ spectrum, this absorption appears mostly as a doublet 570, 580 cm^{-1}. Another strong band occurs in the region around 605 cm^{-1}. When compared with the $Ca_3(PO_4)_2$ spectrum, these bands can be attributed to the absorptions of the deformation vibrations of P-O bonds. All the phosphates studied exhibit the most intensive absorption in the region of 1030-1100 cm^{-1}, and in this region, too, usually two bands are observed, of which that at the lower wave length has always a much greater half-width. These bands belong to antisymmetrical stretching vibrations of P-O bonds. The band in the region of 970 cm^{-1}, present in all the phosphate spectra corresponds to the absorption of the symmetrical stretching vibration of P-O bonds. The other bands observed in the rock phosphate spectra are mostly due to vibrations of C-O and/or Si-O bonds. This concerns e.g. the characteristic doublet at 1430 and 1470 cm^{-1} that appears in the spectra of all the phosphate samples. These particular bands belong probably to stretching vibrations of C-O bonds. Additional bands due to C-O bonds are observed in the region of 870 cm^{-1} and around 720 cm^{-1}. Weak bands in the region of 650-690 cm^{-1}, which occur particularly in the spectra of phosphates D and E, are probably caused by the presence of silicates for they correspond to vibrations of Si-O bonds. The main differences among the IR spectra of the phosphates studied consist in a different number of weak bands in the region of 1200-1400 cm^{-1}.

The so-called CO_2-index is a value characterizing in a certain manner the presence of carbonate ions in the apatite structure of rock phosphates; CO_2-indices were calculated on the basis of the IR spectra according to the method suggested in (7). For this purpose the phosphates had been extracted by the Silverman solution before their IR spectra were measured. The CO_2-index values of the individual phosphates studied are shown in Table 4.

Table 4

CO$_2$-index of rock phosphates [a/]

Phosphate	n [b/]	CO$_2$-index [c/]	Variation range [d/]
A	3	0.527	0.510 - 0.540
B	6	0.243	0.235 - 0.248
C	5	0.573	0.560 - 0.597
D	5	0.554	0.549 - 0.561
E	3	0.503	0.494 - 0.512
F	3	0.304	0.302 - 0.306
G	4	0.287	0.276 - 0.298
H	3	0.457	0.431 - 0.473
I	3	0.141	0.140 - 0.142

a/ CO$_2$-index 0.5 $(I_1 + I_2) / I_3$, where $I_{1,2}$ - intensity of C-O bands in the region of 1450 cm^{-1}, I_3 - intensity of P-O band in the region of 605 cm^{-1}.

b/ n-number of measurements

c/ arithmetic mean of n values

d/ minimum and maximum values of CO$_2$-index.

A modified BET method was employed to measure the values of specific area, and helium and mercury densities of the studied rock-phosphates. The results, obtained with the -0.16 + 0.1 mm fraction, are given in Table 5.

Table 5

Specific area and He and Hg densities of
rock phosphates (-0.16 + 0.1 mm fraction)

Phosphate	He density (g/cm^3)	Hg density (g/cm^3)	Specific surface m^2/g
A	3.161	2.035	23.5
B	3.202	2.607	2.6
C	3.481	2.525	22.0
D	4.702	2.518	24.2
E	3.175	2.423	23.6
F	3.231	2.516	2.0
G	4.269	2.651	5.3
H	3.224	2.579	17.8
I	3.302	2.800	1.3

While the density values, especially in the case of Hg densities, do
not differ substantially, marked differences exist in specific surfaces
of the phosphates studied. Besides, specific surfaces were also measured
for the other fractions of each of the samples and thus the respective
dependences of specific surface area on particle size were determined.
Generally, specific surface area of a given phosphate is increasing as
the size of particles is reduced. The values of specific surface area
obtained were compared with published data and it was found that the
results depend on the experimental method used. E.g. our values are
fairly close to those published by ANDO (9, 10) who, too, was using the
BET method for the specific surface area measurement.

The volume and distribution of pores according to their radius in the
phosphates studied were determined by the porosimetric method. The
measurements were carried out for all fractions of the phosphates and
included macropores as well as transition pores (2000 - 20 Å). An
extensive experimental evidence was gathered of which only a few results
are presented in this paper. It was found that there are marked differences
in the shapes of the distribution curves obtained with phosphates from
the various deposits. Nevertheless, the changes in the particle size have
similar effect. The smallest volume of pores is observed in particles
larger than 0.16 mm, their volume of macropores being insignificantly
small or zero. The volume of transition pores (i.e. r = 2000 Å and less)
is increasing in the -0.16 + 0.1 mm fraction and also the volume of
macropores is more appreciable. In the finest fraction (-0.1 mm), however,
the volume of macropores is rising substantially. Table 6 shows the volumes
of macropores and transition pores in the phosphates studied. Also shown
in the Table 6 are the volumes and volume ratios of pores whose r is
smaller than 600 Å.

Table 6

Porosity of rock phosphates (fraction -0.16 + 0.1 mm)

Phosphate	Vol. of macro- and transition pores (cm^3/g)	Vol. of pores of $r \leq 600$ Å (cm^3/g)	Vol. ratio of pores, of $r \leq 600$Å (%)
A	0.1545	0.1395	90.3
B	0.0750	0.0585	78.0
C	0.0685	0.0615	89.8
D	0.1720	0.1095	63.7
E	0.0880	0.0700	79.5
F	0.0295	0.0100	33.9
G	0.1620	0.1080	66.7
H	0.1060	0.0860	81.0
I	0.0250	0.0070	28.0

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Further, the rock-phosphates were studied by means of the DTA and TGA methods. In most cases the thermograms reveal two main changes, the first of which (at temperatures below 100°C) corresponds to the removal of moisture and volatile organic substances, and the other, occurring at around 720°C, is connected with the release of CO_2.

The following criteria have been adopted for appraising the reactivity of rock-phosphates : the solubility in citric acid and in dilute mineral acids. The former is determined according to a conventional method. A standard amount of the phosphate tested is shaken with a large excess of 2% citric acid for 30 min. The resulting suspension is filtered and the P_2O_5 contained dissolved in the filtrate is determined by the Lorenz method. The ratio of P_2O_5 thus determined to total P_2O_5 in the phosphate sample is called CAP. The found values of CAP are given in Table 7.

Table 7

Solubility of rock phosphates in 2% citric acid
(fraction -0.16 + 0.1 mm)

Phosphate	Total P_2O_5 content (%)	CA-soluble P_2O_5 (%)	CAP (%)
A	32.8	10.2	31.2
B	34.0	4.4	13.0
C	29.3	11.0	37.6
D	28.3	10.3	36.6
E	32.7	9.8	30.0
F	34.2	5.3	15.6
G	35.3	7.8	22.2
H	32.5	7.8	23.8
I	39.8	1.7	4.3

As mentioned earlier, the other adopted criterium of reactivity of rock phosphates is their solubility in various mineral acids (HNO_3, H_2SO_4, H_3PO_4). This approach to testing was suggested earlier by some authors (10,11) but the experimental method used in the present work was different. The decomposition of a rock-phosphate by mineral acids is accompanied by regular changes in the conductivity of the reacting systems. These changes in the conductivity were continuously measured by a conductoscope and automatically recorded (an example of the recorded curve is shown in Fig.1). It was proved that the shape of such conductometric curves is identical to the shape of curves expressing the dependence of the content of dissolved P_2O_5 in the solution on time. When an actual P_2O_5 concentration at the end of a measurement is known, it is possible to read off the changing concentration values directly from the conductometric curve. To secure the objectivity in comparing reactivities, it was necessary to choose such values of the reaction time that would guarantee

that none of the phosphate would be completely decomposed. The
P_2O_5 concentration in the solution is then determined at the chosen
time. The ratio of P_2O_5 thus determined to total P_2O_5 in a particular
phosphate represents the degree of phosphate solubility in a given acid
at the given time. The solubility values obtained in this manner are a
basis for comparing the reactivities of the phosphates studied. Table 8
shows the solubility data as obtained by the described method.

The effects of calcination on the properties and reactivity were studied
with some of the rock phosphates (A,C,E,F,H,I). Based on the results
of the DTA and TGA analyses, the following calcination temperatures were
selected : 500, 700 and 900°C. While the properties of phosphates F and I
changed only slightly, phosphates A,C,E and H were affected markedly.
The most interesting results obtained by the investigation on calcined
phosphates are presented in Tables 9, 10 and 11. Figure 2 shows diagram-
matically the effect of calcination temperature on the value of lattice
constant a of phosphates.

Table 8

Degree of rock phosphates solubility in 0.25 N mineral
acids at 25°C (fraction −0.16 + 0.1 mm)

Phosphate	Degree of phosphate solubility (%)					
	HNO_3		H_2SO_4		H_3PO_4	
	30	60	30	60	30	60
			reaction time (sec)			
A	58.2	82.8	37.5	53.6	27.2	41.7
B	33.3	56.1	16.8	28.7	9.0	14.9
C	55.7	78.2	37.2	54.4	26.3	42.9
D	74.3	88.9	52.1	74.2	41.3	54.2
E	62.3	84.2	37.8	54.1	25.7	29.8
F	21.5	40.6	11.9	22.8	6.9	11.8
G	42.6	60.9	24.0	36.9	14.8	22.5
H	34.1	52.1	20.5	35.3	7.9	17.0
I	4.9	7.4	3.1	4.6	1.0	1.5

Table 9

Effect of calcination on chemical composition and specific
surface area of rock phosphates (fraction −0.16 + 0.1 mm)

Phosphate	P_2O_5 (%)	H_2O (%)	F (%)	CO_2 (%)	Sp. surface m^2/g
A_1	32.8	2.61	3.78	4.35	23.5
A_2	33.2	−	4.01	3.97	20.0
A_3	34.2	−	4.17	3.03	13.7
A_4	35.1	−	4.25	0.44	0.5

Table 9 (continued from p. 9)

Phosphate	P_2O_5 (%)	H_2O (%)	F (%)	CO_2 (%)	Sp. surface m^2/g
C_1	29.3	3.83	3.61	5.64	22.0
C_2	29.8	-	3.68	4.89	12.9
C_3	31.0	-	3.70	3.17	2.0
C_4	31.6	-	3.77	0.41	0.5
E_1	32.7	2.54	3.49	5.35	23.6
E_2	34.1	-	3.85	4.23	10.4
E_3	35.0	-	4.08	2.98	4.9
E_4	35.2	-	4.18	0.48	0.4

Subscripts : 1 - non-calcined phosphate

2 - phosphate calcined at 500°C

3 - phosphate calcined at 700°C

4 - phosphate calcined at 900°C

Table 10

Solubility of calcined phosphates in 2% citric acid

Phosphate	Calcination Temperature (°C)	Total P_2O_5 content (%)	CA-soluble P_2O_5 (%)	CAF (%)
A	500	33.4	9.8	29.4
	700	33.9	7.3	21.5
	900	34.6	4.5	13.0
C	500	30.3	10.2	33.7
	700	31.6	5.9	18.9
	900	32.3	5.7	17.6
E	500	33.5	9.5	28.4
	700	34.5	5.5	16.0
	900	35.5	3.8	10.7
F	500	34.8	5.6	16.1
	700	34.6	5.7	16.5
	900	35.2	5.6	15.9
H	500	32.7	7.2	22.0
	700	33.2	7.1	21.4
	900	34.4	6.4	18.6
I	500	38.2	2.0	5.3
	700	38.5	2.1	5.5
	900	38.4	2.1	5.5

Table 11

Effect of calcination temperature on the degree of solubility
of phosphate C in dilute mineral acids (0.25 N) at 25°C.

Temp. of phosphate C calcination (°C)	Degree of phosphate solubility (%)					
	HNO_3		H_2SO_4		H_3PO_4	
	Reaction time (sec)					
	30	60	30	60	30	60
500	51.3	74.2	35.4	52.8	22.4	34.7
700	40.2	62.3	27.1	42.0	16.0	26.0
900	34.8	57.4	18.7	31.7	11.3	18.3

Mathematical correlations

The least square method was used to verify the linear relationships
among the studied factors. The results of the mathematical treatment
of experimental data are presented in Tables 12, 13 and 14. Summarized
in these tables are the constants a and b, standard deviations σ_a,
correlation coefficents r, and residual standard deviations σ_r for
linear regression of the type y = ax + b.

Table 12

Mathematical correlations among physical properties of rock
phosphates and their chemical composition

y	x	a	b	σ_a	r	σ_r
y_1	x_1	-0.010	9.382	0.0020	0.880	0.011
	x_2	-0.013	9.386	0.0013	0.965	0.006
y_2	x_1	1.337	11.148	0.2434	0.901	1.369
	x_2	1.661	10.717	0.1514	0.972	0.740
	x_3	-128.222	1214.392	10.9244	0.976	0.694
y_3	x_1	4.373	-0.911	0.9522	0.866	5.357
	x_2	5.414	-2.266	0.7974	0.932	3.896
	x_3	-405.238	3802.340	71.3623	0.906	4.531
	x_4	3.195	-36.205	0.4406	0.939	3.677

y_1 = lattice constant $\underline{a}$

y_2 = half-maximum breadth of diffraction line (123)

y_3 = specific surface

x_1 = CO_2 content before extraction by ammonium citrate

x_2 = CO_2 content after extraction by ammonium citrate

$x_3 = y_1$

$x_4 = y_2$

Table 13

Mathematical correlations among rock phosphate solubilities
in 2% citric acid and their physical properties

x	a	b	$\mathscr{6}_a$	r	$\mathscr{6}_r$
x_1	51.94	-56.86	36.01	0.479	10.43
x_2	148.78	7.25	285.94	0.193	11.65
x_3	152.54	7.84	25.57	0.914	4.82
x_4	5.08	7.00	0.96	0.894	5.32
x_5	5.85	6.64	0.59	0.966	3.11
x_6	141.38	-5.23	11.69	0.980	2.37
x_7	18.99	-30.72	1.53	0.981	2.35
x_8	21.41	-37.13	2.68	0.956	3.56
x_9	4.89	5.74	0.50	0.970	2.93
x_{10}	-467.24	4392.84	61.56	0.944	3.91
x_{11}	3.67	-32.83	0.40	0.961	3.32
x_{12}	1.02	10.53	0.16	0.918	4.70
x_{13}	158.41	13.54	70.25	0.677	8.78
x_{14}	0.38	-0.01	0.11	0.825	6.75

x_1 = CaO/P_2O_5

x_2 = F/P_2O_5

x_3 = CO_2/P_2O_5

x_4 = CO_2 content before ammonium citrate extraction

x_5 = CO_2 content after ammonium citrate extraction

x_6 = $(CO_2 + F)/P_2O_5$

x_7 = $(CO_3 + F)/10\ CaO$ before extraction

x_8 = $(CO_3 + F)/10\ CaO$ after extraction

x_9 = $CO_2 \pm (F_{real} - F_{ideal})$

x_{10} = $\underline{a}$

x_{11} = half-maximum breadth of diffraction line (123)

x_{12} = specific surface

x_{13} = volume of pores of $r \angle$ 600 Å

x_{14} = volume ratio of pores of $r \angle$ 600 Å

Table 14

Mathematical correlations between reactivity of rock phosphates
with dilute mineral acids and their physical properties

y	x	a	b	σ_a	r	σ_r
y_1	x_1	282.15	-17.33	43.50	0.93	8.84
	x_2	9.46	7.13	1.41	0.93	8.56
	x_3	-808.41	326.38	205.90	0.85	13.10
	x_4	6.63	-59.39	1.26	0.90	10.50
	x_5	121.25	-5.36	25.95	0.88	11.51
	x_6	1.80	18.55	0.40	0.87	11.97
	x_7	0.66	-1.89	0.26	0.68	16.97
y_2	x_1	196.67	-15.34	32.96	0.92	6.70
	x_2	6.60	1.75	1.07	0.92	6.54
	x_3	-566.70	225.43	148.34	0.84	9.42
	x_4	4.72	-46.10	0.86	0.90	7.21
	x_5	87.58	-8.16	17.05	0.89	7.57
	x_6	1.31	9.01	0.26	0.80	7.76
	x_7	0.42	-1.99	0.20	0.62	12.92
y_3	x_1	159.07	-16.22	33.10	0.89	6.72
	x_2	5.29	-2.27	1.11	0.86	6.79
	x_3	-423.97	166.41	150.20	0.78	9.53
	x_4	3.64	-38.44	0.95	0.83	7.90
	x_5	69.17	-9.79	17.36	0.84	7.71
	x_6	1.04	3.71	0.26	0.83	7.77
	x_7	0.29	-2.06	0.19	0.51	11.98

y_1 = degree of solubility of phosphates in 0.25N HNO_3 at 25°C, time of decomposition 30 sec.

y_2 = degree of solubility of phosphates in 0.25N H_2SO_4

y_3 = degree of solubility of phosphates in 0.25N H_3PO_4

x_1 = $(CO_2 + F)/P_2O_5$

x_2 = $CO_2 \pm (F_{real} - F_{ideal})$

x_3 = $\underline{a}$

x_4 = half-maximum breadth of diffraction line (123)

x_5 = CO_2 - index

x_6 = specific surface

x_7 = volume ratio of pores of r $\angle$ 600 Å

Discussion

Our research efforts have been aimed primarily at establishing the relationships between the reactivity of rock phosphates and their chemical as well as physical properties. It is, however, necessary to understand also the relations among their other properties, particularly between their structure and chemical composition. These problems were studied earlier (6,7,9,13); e.g. LEHR and McCLELLAN conducted a detailed crystallo chemical research on rock phosphate which gave ample evidence for their conclusions (14). Since our experiments have confirmed these conclusions, they will be dealt with only to an extent such as necessary with respect to the discussion of rock phosphate reactivity.

It follows from Table 1 that the CO_2 contents exhibit the relatively largest differences among the individual components in the phosphates. These differences are attributed to the geologic origin of the respective rock; the CO_2 content is highest in sedimentary phosphorites (e.g. phosphates C, E) and lowest in igneous apatites (phosphate I). The values of lattice constants a (Table 3) indicate the relationship between the rock phosphate structure and its CO_2 content. They are markedly lower (9.320 - 9.350 Å) in phosphates with a high CO_2 content than in phosphates containing very small amounts of CO_2 (a = 9.372 and 9.390 Å in the phosphates F and I, resp.). The correlation between the CO_2 content and the a value becomes even more apparent when phosphates are preliminarily treated by the Silverman solution, so that only carbonate ions present in the apatite lattice remain in the phosphate studied (Table 2). This is explained by the fact that the rock phosphate is a mixture of several minerals; the essential mineral is apatite and its structure is described by the lattice constants a and c, which are determined by the X-ray method. The a and c values of pure fluorapatite are 9.387 and 6.882 Å, resp. A comparison of these values with our experimental data reveals that cells of apatite crystals in the rock phosphates studied are prolonged in the direction of the c axis, while the a axis is shorter. This is due to the presence of carbonate ions in the apatite lattice, which impairs its original structure and brings about its deformation. The extent of such a deformation is naturally more appreciable when the content of "foreign" carbonate ions in the lattice is higher. This interpreted dependence of the degree of the apatite structure deformation on the content of CO_2 is supported by an exact mathematical relation (Table 12). The high value of the correlation coefficient for linear regression between the lattice constant a and the CO_2 content confirms convincingly the correctness of our conclusions.

The dependence of the lattice constant a on the carbonate content can be also found with calcined phosphates. The CO_2 content decreases as the calcination temperature increases and, simultaneously, the a value grows (Fig.2), which is obviously due to a recrystallization process.

The effect of the presence of CO_2 on the size of primary crystallite grains is virtually the same. Their size is indirectly proportional to the half-maximum breadth of the diffraction line (123) as shown in Table 3. The dependence becomes more distinct in the case of samples. whose CO_2 content is adjusted by the preliminary treatment with ammonium citrate; this is also confirmed by the values of the correlation coeffi-cients (Table 12). The lower the CO_3^{2-} content in the apatite lattice of rock-phosphate, the larger and better developed are crystals formed. The primary crystallite size is naturally related directly with the crystal structure and this dependence is also proved by the high correla-tion coefficient for the diffraction line (123), half-maximum breadth and the lattice constant a , as shown by the dependence of y_2 on x_3 in Table 12. The effect of calcination is the same as in the above cases discussed : when the calcination temperature increases and the CO_2 content decreases, the size of primary crystal grains in calcined rock-phosphates grows (Table 10).

The specific surface area is another important property of rock-phosphates. It follows from a comparison of Tables 1, 2 and 5, that the specific surface area is also affected by the CO_2 content. The dependence has been proved mathematically and also in this case the higher value of the correlation coefficient indicates a better correlation between the specific surface area and the CO_2 content after the preliminary treatment with ammonium citrate. This proves, at the same time, that there is a correlation between the specific surface area and the phosphate structure, irrespective of whether it is expressed by the lattice constant a or by the size of primary crystal grains. The values of correlation coefficients, however, give evidence of a more substantial influence of the crystal grain size. Actually, the sedimentary phosphorites (e.g. A,C,D) with a microcrystalline structure exhibit a far larger specific surface area than igneous apatites (phosphate I). It follows from the observations discussed that the calcination will affect markedly the value of the specific surface area when the CO_2 content decreases and the size of primary crystal grains grows. This effect is most appreciable in phos-phates calcined at 900°C; the value of specific surface area of samples calcined at 900°C drops to or even below that of the phosphate I.

The most important conclusion that can be drawn from the above observa-tions is that the high values of correlation coefficients as established for the respective linear regressions confirm the existence of fairly good correlations between the characteristics examined. The lattice constant a, half-maximum breadth of the diffraction line (123), the specific surface area and the CO_2 content are mutually correlated and interchangeable when relations between the reactivity of rock phosphates and their properties are sought for.

When assessing the reactivity of rock phosphates and examining the effects of various variables thereupon, it is necessary to keep in mind that "reactivity" is a relative concept whose value depends largely on the method of its definition. The solubility values of rock phosphates

in 2% citric acid as well as the degree of their solubility in dilute
mineral acids during a given period of time have been adopted as the
measure of reactivity for the purpose of our studies (Tables 7, 8 .

Phosphates A, C, D and E exhibit the highest reactivity, while phosphate 1
is quite obviously the least reactive one. This confirms the dependence
of the rock phosphate reactivity on its chemical composition and some
other characteristics discussed earlier. A mathematical treatment of
these relations and the values of the corresponding correlation coefficients
confirm quite clearly the validity of correlations between some of the
properties (Table 12, 13, 14) but, on the other hand, they contradict
the existence of correlations between some other characteristics.

The investigations of the effects of the composition of rock phosphates
on their reactivity have confirmed, in accordance with literature 6,7,9.
10,11), that the reactivity does not depend on the CaO/P_2O_5 or F/P_2O_5
ratios. On the other hand, the values of the correlation coefficients
prove that the reactivity does depend on the content of carbonates or or
the CO_2/P_2O_5 ratio. In the case of CO_2, it is practically unimportant
whether the total original carbonate content is considered or if the
phosphate has been subjected to a preliminary extraction by ammonium
citrate, by which virtually all carbonate ions are removed leaving only
those included in the lattice of the principal phosphatic mineral - apatite.
The chemical composition of rock phosphates differs more or less from the
composition of the pure fluorapatite. This is mostly due to the presence
of carbonate ions in the apatite lattice of phosphates but also to the
excessive fluorine content as related to the amount of calcium. Therefore,
certain terms, expressing the deviations in the chemical composition of
rock phosphates from that of pure apatite were established and the effects
of these deviations on the phosphate reactivity were studied. High values
of the corresponding correlation coefficients confirm that the dependence
of reactivity on the deviations thus expressed is virtually linear. This
can also be seen in Fig. 3, showing diagrammatically the dependence of
phosphate reactivity on the molar ratio $(CO_2 + F)/P_2O_5$. The dependence
on the rock phosphate reactivity (measured with dilute mineral acids) on
the deviations in their composition is most distinct when related to the
term $\%CO_2 + \%F_{real} - \%F_{ideal}$ (% by weight); in our opinion, this term is
very suitable for expressing the deviations in the composition of phos-
phates. $F_{id.}$ is calculated as $\% F_{id.} = \% F_{real} \cdot 2F/6P$ (by weight), where
F and P are the resp. atomic weights. It follows from the experimental
evidence that the total carbonate and fluorine contents influence the
rock phosphate reactivity substantially, while the fluorine or calcium
contents alone are insignificant.

The effects of rock phosphate structure on their reactivity have been
confirmed in a similar way. This dependence is particularly distinct
in the case when the reactivity is based on the action of dilute citric
acid. The high values of the correlation coefficients (0.94 and 0.96)
indicate a linear regression between CAP and the size of the crystal
axis a or the half-maximum breadth of the diffraction line (123), resp..

It may be stated that rock phosphate reactivity decreases when the
length of the crystal axis a and the size of primary crystal grains grow.
In other words, the closer the structure of rock phosphates to that of
fluorapatite, the slower their decomposition. This conclusion is in a
perfect agreement with the correlation between the structure of phosphates
and their chemical composition. The validity of the correlations between
the reactivity of rock phosphate and their chemical composition and
structure has been also confirmed by the high value of correlation
coefficients as established for the dependence of the reactivity of the
CO_2-index of rock phosphates. The CO_2-index, too, expresses in a certain
way both the chemical composition and structure of rock phosphates.

A comparison of the corresponding data also shows clearly the dependence of
the reactivity on the specific surface area of the phosphates studied
(Tables 5, 7, 8).   Rock phosphate reactivity decreases with
decreasing specific surface. This is particularly conclusive in the case
of phosphate I : its limited reactivity is in accordance with its very
low specific surface area. Also this dependence has been confirmed by
establishing the corresponding correlation coefficient. On the contrary,
no satisfactory correlation could be found when examining the dependence
of the reactivity on the volume of macro- and transition pores or their
cumulative volume. Caro and Freeman have stated that only certain pores,
i.e. those with r < 600 Å, play a decisive role in the phosphate decom-
position process so that their share in the total volume of pores is
very important (3). The values of the correlation coefficients resulting
from our calculations of the correlation between phosphate reactivity and the
volume or relative volume of these pores (r < 600 Å) are rather low and
they actually contradict the existence of the correlation between the
reactivity and distribution of pores according to their radius. Even
multiple correlations involving some other factors have not given any
better result.

All the above observations have been confirmed conclusively by the
results obtained when studying the effects of calcination on rock phos-
phate reactivity. The rising temperature of calcination brings about
a decrease in the CO_2 content, an increase in the length of the crystal
axis a and an increase in primary crystallite size as well as a decrease
in the specific surface area (Table 9, Fig. 2). Consequently, the
reactivity of the calcined phosphates should decrease; the experiments
have proved the correctness of this assumption (Tables 10, 11).

It may be concluded from the discussed facts that there are two essential
factors affecting the rock phosphate reactivity under given conditions.
The first factor is the crystallographic structure and chemical composi-
tion of the elementary cells of apatite - the mineral constituent in
rock phosphates. It has been found that the greater the deviation in
the structure and composition of such a cell, the higher the phosphate
reactivity. These deviations are the measure of the degree of imperfec-
tion of a given lattice and thus also of its energy content. In an ideal
crystal all the ions are arranged in the energetically most advantageous
positions and, therefore, substantially more energy is needed for des-
troying it than in the case of an imperfect crystal, e.g. the apatite
crystals in rock phosphates. The phosphates studied A, C, D and E, for

instance, contain appreciable amounts of carbonate ions, substituting
the phosphate ions in the apatite lattice. The carbonate ions, however,
are not situated exactly in the positions occupied originally by
phosphate ions and since electroneutrality has to be maintained, either
additional fluorine ions may be present or calcium ions may be partly
substituted by alkali metal ions. All these factors contribute to an
energetic lability of such crystals and thus also to their higher
reactivity. A contrary situation is encountered in the case of phosphate I
or phosphates calcined at 900°C.

The second essential factor is the specific surface area of rock phosphates.
This fact is well known (1, 2) and it is associated with the nature of
the decomposition process of a phosphate by an acid, which is essentially
a surface reaction. It must be mentioned, however, that our experiments
were carried out with acids at very low concentrations, so that the
effect of specific surface area can be fully appreciated. The forming
salts do not hinder the process and even the effect of calcium sulphate
precipitating when sulphuric acid is used is much smaller when compared
with the process carried out under actual technological conditions.
There are obviously also other factors affecting phosphate reactivity.
When reactivity was assessed on the basis of the action of dilute
mineral acids, higher values of the correlation coefficients were found
for its dependence on the total content of CO_2 than for the value of
the lattice constant $\underline{a}$. This indicates that those carbonates present in
a rock phosphate in the form of separate minerals (e.g. calcite or
dolomite), affect favourably the phosphate decomposition process in a
large volume of a given solvent since the carbon dioxide released
attacks the aggregation force among other crystal grains. Such a concept,
however, applies probably only in the case of decomposition by dilute
acids.

It may be concluded that the reactivity of a given rock phosphate can be
assessed on the basis of the knowledge of certain factors. Among such
factors, the following should be mentioned in particular : lattice
constant $\underline{a}$, half-maximum breadth of the diffraction line (123), molar
ratio $(CO_2 + F)/P_2O_5$ or the factor $CO_2 \pm (F_{real} - F_{ideal})$, CO_2-index and
specific surface area. These conclusions are fully justified when
evaluating rock phosphate reactivity to dilute acids. The decomposition
conducted under the conditions of a commercial scale process is naturally
complicated by important additional factors (e.g. gypsum precipitation
on the surface of phosphate particles). Nevertheless, in our opinion
the knowledge of the discussed relationships between the reactivity of
phosphates and their properties represents a sound basis for characteri-
zing and evaluating the phosphates.

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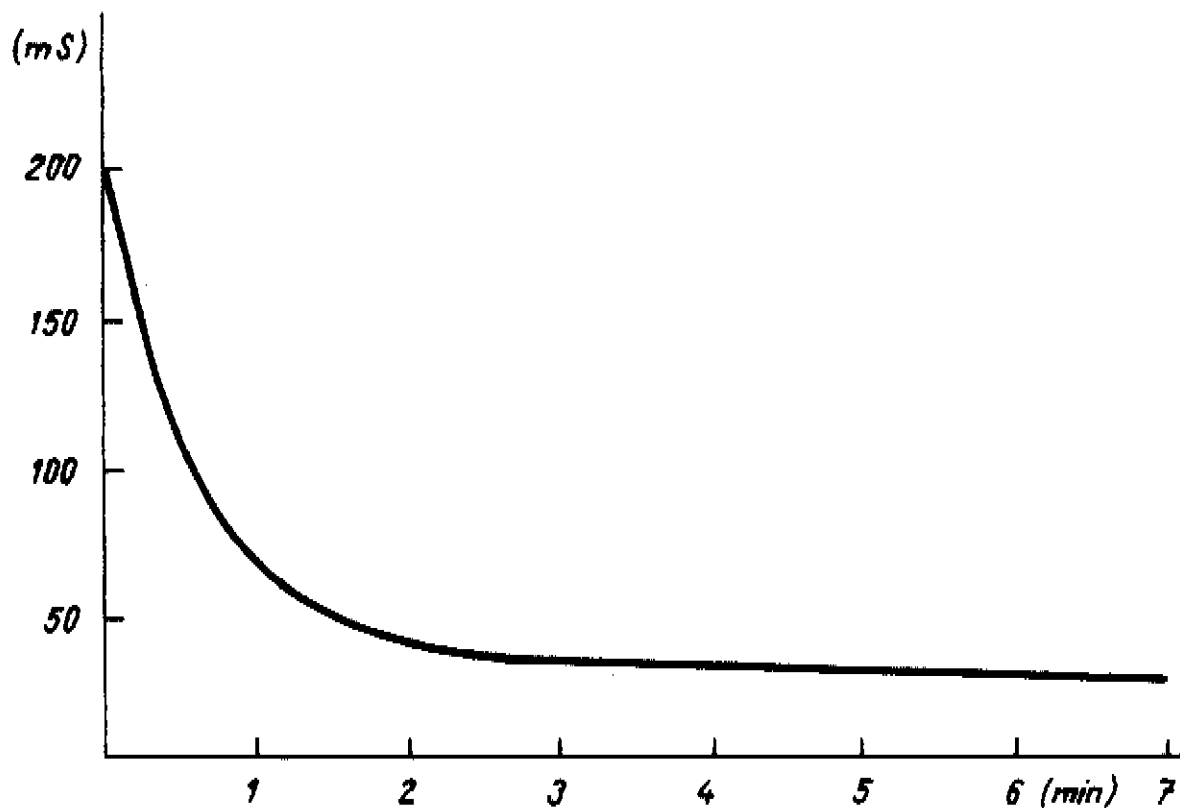
Fig. 1 - Time-dependence of reaction solution conductivity
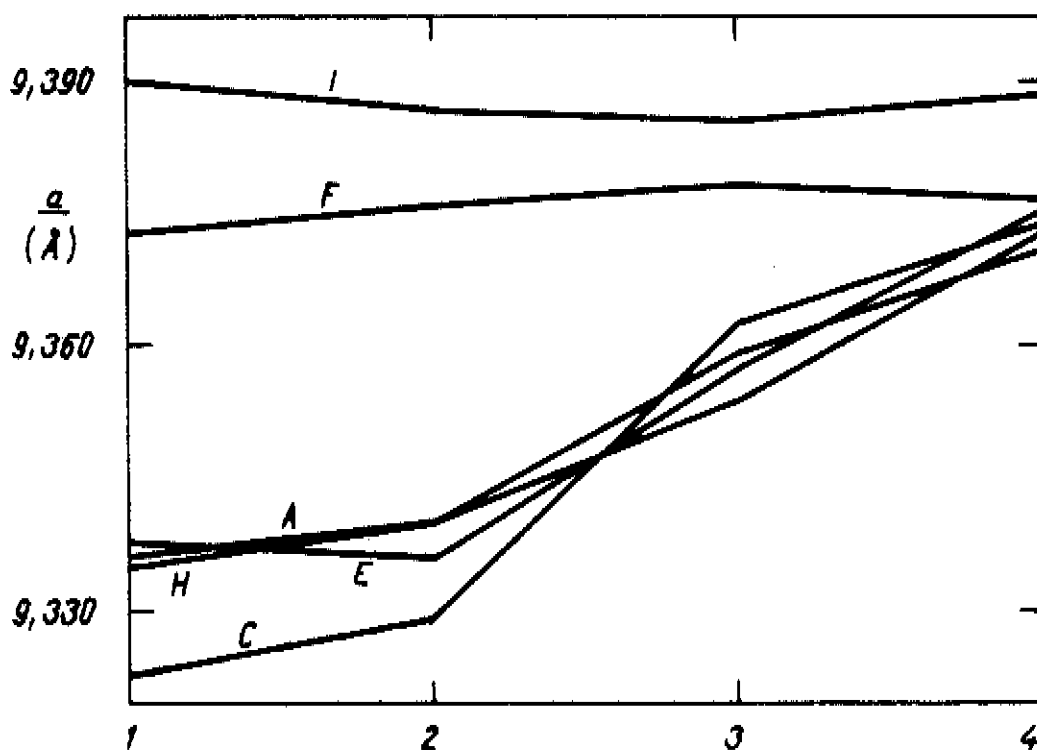during decomposition of phosphate B by 1N HNO$_3$ at 25° C

Fig. 2 - Effect of calcination temperature on lattice
constant a of raw phosphates
1 - original raw phosphate
2 - phosphate calcined at 500° C
3 - phosphate calcined at 700° C
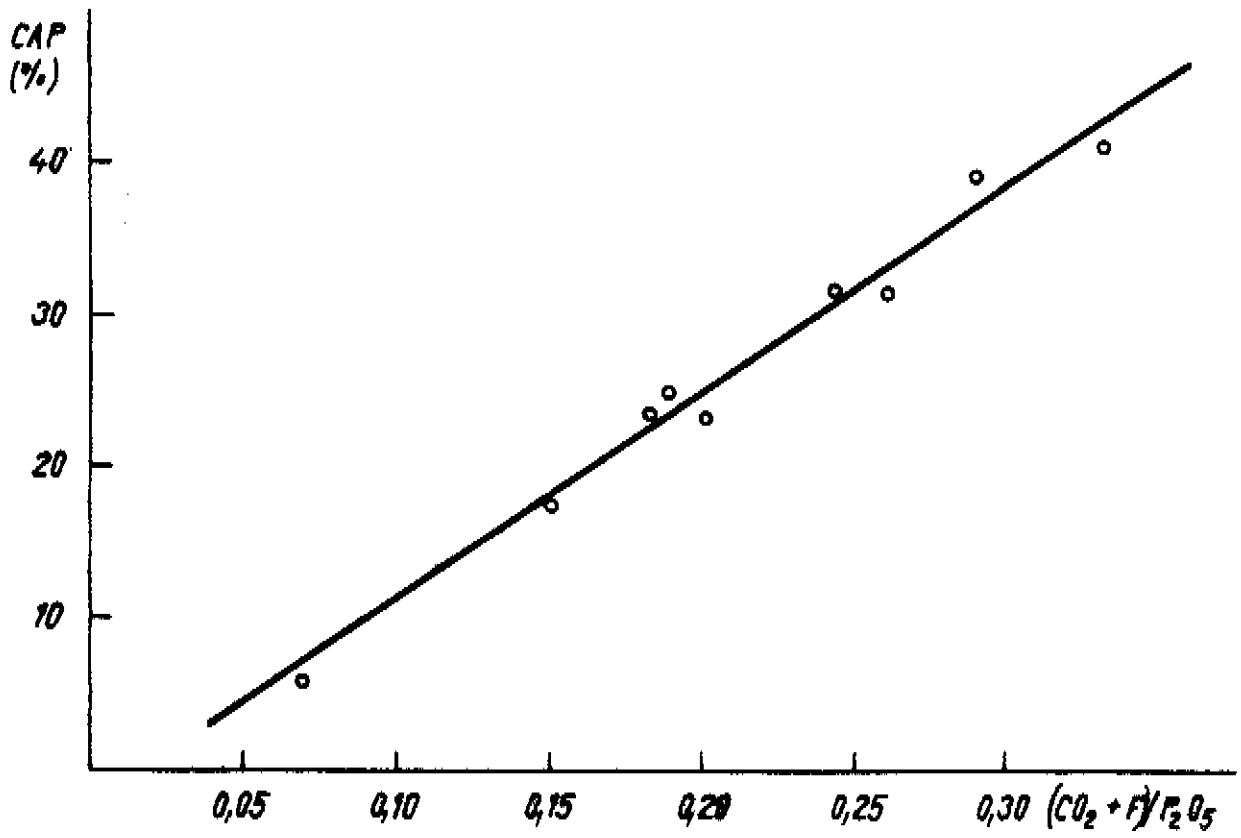4 - phosphate calcined at 900° C

Fig. 3 - Dependence of raw phosphates reactivity
(expressed as CAP) on the ratio $(CO_2+F)/P_2O_5$

COMMUNICATION N° 12

Dr. HEGNER (Research Institute of Inorganic Chemistry, Czechoslovakia)

Let me introduce briefly our paper presenting some results of investi-
gations carried out in the Research Institute of Inorganic Chemistry,
which are devoted to the acquiring of a better knowledge of some
fundamental properties of raw phosphates. Our interest in this problem
stems primarily from the fact that here in Czechoslovakia, like in many
other countries, the industry has to process various very different raw
materials in their production of phosphatic fertilizers and most
effective utilisation of these very costly imported materials has
become a matter of serious concern of our producing plants and,
consequently,of the researchers.
In the initial stage of our studies we were examining some chosen physico-
chemical characteristics of various phosphates treated in Czechoslovakia.
We were studying chemical composition of the selected phosphates, their
crystallographic structure, that is the lattice constants value and
size of the primary crystallites, their surface structure/specific
surface area, helium and mercury densities, distribution of the pore
radii size /; their infra-red spectra as well as the differential thermal
analysis: and thermogravimetric curves.
An evaluation of the obtained experimental results allowed us to draw
certain generalized conclusions, according to which every phosphate may
be characterized by one of the following physico-chemical parameters :
lattice constant a, size of primary crystallites, specific surface area
and the content of carbonate ions in the apatité lattice of phosphates /i.e.
the CO_2 content as determined after an extraction by ammonium citrate /
or by the CO_2 index as assessed from IR-spectra. At the same time we
have been able to demonstrate that the studied parameters are mutually
correlative.
For example, Figure 1 documents the relation between the values of lattice
constants a and the content of CO_2.
The per cent values of CO_2 content, determined after extraction by
ammonium citrate, are plotted on x-axis, the lattice constants a in A
are plotted on the y-axis.
As the next stage, we have been studying the reactivity of rock-phosphates
and its dependence on the above mentioned parameters. The adopted criteria
for appraising the reactivity of phosphates are their solubility in citric
acid and in dilute mineral acid, which is measured under standard
conditions. The following diagrams are selected to illustrate but some
of great number of the obtained results.
Figure 2 shows the effect of raw phosphates origin, i.e. mineralogical
type, on the rate of their dissolution by dilute sulphuric acid. The
differences in the rates of decomposition of the individual phosphates can
be seen very clearly from the diagram : the least reactive is phosphate L,
whose composition is fairly close to that of pure fluoroapatite.
The next diagram - Figure 3 - demonstrate the effect of particle size of
the given phosphate type on the rate of its dissolution by dilute sulphuric

acid. /C_a -0.16 mm oversize, C_b -0.10mm to 0 16mm fraction, C_c -0.1mm
screen undersize and C_d - product obtained by grinding the original
phosphate so that the whole sample passes through the 0,1 mm screen.
The coarsest fraction decomposes most slowly, whereas the finely
ground phosphate dissolves most readily.
Figure 4 shows the dependence of decomposition rate of one phosphate
studied on the concentration of nitric acid. It is obvious that the
rate of decomposition grows with increasing the acid concentration.
Similar dependence as these shown in Figures 3 and 4 was found also
with the other phosphate types and this, too , documents considerable
differences in the reactivity of different types of phosphates.
When analysing the linear correlations among the various examined
factors, we have proved that the reactivity of phosphates, as defined
for the purpose of our studies, depends on the earlier enumerated
parameters of rock-phosphates.
This may be exemplified by Figure 5 , which shows the dependence of
the rate of phosphates dissolution in dilute nitric acid on their chemical
composition. Analogically, it is possible to demonstrate the effect
of primary crystallites.
The differences in their size are documented by electron microphotographs/
magnification 3 000 times / of phosphates A and I; the primary crystal
grains in the phosphate I / see Figure 6 / are markedly larger than those
in the phosphate A / see Figure 7 /, the composition and structure of the
latter differing considerably from those of pure fluoroapatite.
The presented facts as well as the other extensive evidence in our inves-
tigations enables us to state quite conclusively that the reactivity of
raw phosphates is very closely connected with their crystallographic
structure and chemical composition. The closer the structure and the
composition of the main mineral component of rock-phosphates i.e. apatite,
to those of pure fluorapatite, the lower is the reactivity.
The above conclusions have been fully confirmed also by results of our
studies of the effects of calcination on the reactivity and some other
properties of phosphates. The rising temperature of calcination brings
about an increase in the length of the crystallographic axis as well as
in size of primary crystallites, while, at the same time, specific surface
area is decreasing.
This can be seen very clearly from Figure 8, in which the calcination
temperature is plotted on the x-axis and specific surface area / 9 cm2 /
on y-axis. It follows from the diagram that at the temperature of
calcination 900° C the value of the phosphates A, C and E drops to that
of the phosphate I.A similar phenomenon has been observed with respect
to the lattice constant Q.
Figure 9 then illustrates the decrease in the rate of decomposition of
phosphate C by the dilute sulphuric acid, as brought about by increasing
the temperature of calcination. Such a decrease in reactivity due to
calcination is given, according to our results, by changes in the values
of the decisive parameters.
This is documented also by Figure 10, demonstrating how the volume of pores
decreases with increasing of the calcination temperature.
Similarly, the ncyt diagrams show the growth of the size of crystallites
in phosphate E as brought about by increasing the temperature of calci-
nation : figure 11 - calcination at 500°C, Figure 12 - 700°C, Figure 13 -
900° C.

The studies, whose essential results have been briefly outlined, can be characterized as modelling under laboratory conditions, which aim at the determination and evaluation of the fundamental processes and relationships. These results, therefore, cannot be applied directly in a plant-scale practice. In our view, however, the continuing extensive studies devoted to the indicated problems will contribute to a better understanding of the properties of various types of raw phosphate materials and, ultimately, they should benefit also the fertiliser industry.

Dr. RITZERT (B.A.S.F., G.F.R.)

As a result of the symptoms of an expanding phosphate shortage, the countries without any domestic ressources are more and more compelled to cover their requirements with all possible ressources.
The need to process phosphate rocks of which one has very little practised experience is becoming increasingly frequent.
Frequently phosphoric acid and nitrophosphate producers have to face unexpected difficulties due to apparently unclarified reasons during phosphate solubilization, gypsum filtration or, as in the case of the Odda process removal of calcium nitrate, steam addition or granulation, during the conversion of the phosphate rock reacted.
Phosphate processing firms use laboratory tests which, however, to be applied to the industrial scale, must be quite comprehensive and can only be used as references for possible difficulties with a considerable personal know-how.
In the paper we have heard how a macroscopic behaviour, namely phosphate solubility in mineral acids, can be very cleverly explained by a microscopic picture derived from very different physical assessments of various phosphate types.
A great part of the paper deals with microscopic transformations on the course of calcination and the resulting changes in the properties of the solution. In industrial practice calcined phosphates only play a secondary role. In practice it appears that sometimes the foam produced in the reaction solution makes the use of pumps difficult and, hence, the retention time in the reaction tank is not determined by the solubility but by gas evolution.
1. You found that the rate of reaction with mineral acids depends on the CO_2/P_2O_5 ratio.
   What is the influence of organic matter, in particular in the case of the reaction with nitric acid? Has it not an accelerating effect or, concerning organic matter, are there inclusions in the crystalline structure?
2. You found a substantial decrease in the rate of reaction when the temperature of calcination increases. Is it not related to the sweetening time for the various temperatures?
3. You use the electrical conductivity of the solution to assess the reaction. The electrical reactivity of a nitric acid reaction solution results from the conjunction of unreacted acids, of the phosphoric acid produced, of calcium nitrate, humic acid, etc...
   Does this method allow to compare the various phosphates or is the colour variation with the heat not a specific research method?

4. You found that the fine phosphate particles are low in P_2O_5 . We
use mostly Florida phosphates. In that case we always found that
coarse particles contain more CO_2 and less P_2O_5. The P_2O_5 content
varies between 32 and 28° . Among all the phosphates you studied,
did you include Florida rock?

M. HEGNER

The first question was about the method we use for our studies.
We choose this conductivity method because it is quick and accurate
enough. We tried it many times and checked it and we are quite sure
that this method can be used for evaluation of different properties of
phosphate rock. I can say it for these samples, we have checked in
our laboratory. Of course there are some limitations of the method.
As you can see during the excursion in our Institute, this method works
very well up to the concentration of mineral acid of 8 to 10 %, then start
many difficulties with foaming of course, but still we succeed to measure
some of the samples of high concentration of acid. But there is a limit
in this method.
The question about the measurement of some effect by dissolution of
phosphate rock. There is a possibility but we are sure that, to understand
the differences between various phosphate types, we need more accurate
methods than when we can use by the usual apparatus. So to this
purpose we use the very exact ultracalorimeter.   The rate of this
is very slow and very difficult but we hope that we can proceed with it
and still our results confirm the conclusion we made from the conductivity
method quite good and they are confirmed with this method.
To the second one, I can say between the samples, we checked also the
properties of Florida phosphate and we can only say that the remarks
of Dr. Ritzert are right. Our observations are about the same.
The third question was about the influence of the time of calcination.
Of course there is an influence but still we have no time to study
this problem more closely and so I can only tell you that by lower
temperatures, it means 500°C, there was influence, it means our samples
were calcinated during just one hour but we observed several times that
the reactivity of calcinated rock, which is calcined longer than one
hour at a temperature of 900°C, decreases. I am sorry I am not able
to answer exactly the fourth question because the influence of organic
substances in phosphate rock is a very difficult problem and we are
looking still for a better method to analyse this material to know what
exact substances are present in samples we have in our work, so we try in
this field but there are no results I can comment.

M. ROGERS (Fertiliser Research Association, New Zealand)

1. I wish to suggest to the authors of this interesting paper that the
physico-chemical properties of phosphate minerals reflect the geological
and geo-chemical processes operating during the formation of the parti-
cular phosphate deposit e.g. primary or secondary sedimentation,
e.g. whether eroded and transported, or an igneous origin such as the
Kola or Phalabowra. These genetic processes decide such physical
properties as porosity and crystallite size and chemical ones like the

carbonate content and the substituents in the apatite lattice.
Therefore would authors please add a key to Table I in their
paper when it appears in the Proceedings, indicating where the 9
samples A to I came from, and their geological age and type
(sedimentary or igneous).

2. My second comment is that Table I is incomplete in that addition
shows the totals of oxides and F listed range from 99.3 % for I to
88.3 % for C. Therefore, like Oliver Twist, I would ask for more
food for thought by way of figures for the alkali metal oxide, Na_2O,
K_2O and alkaline earths Mg C, S_2O as well as SO_2, Carbon and H_2O
content of phosphates A to I. Could the authors arrange for these
to be included in the Proceedings version of their paper.
For comparative purposes I shall be pleased to supply analysed
samples of the oceanic sedimentary phosphates from Nauru and Christmas
Island (Indian Ocean) which are so important to the superphosphate
manufacturers in New Zealand (and Australia). In these apatites
hydroxyl and fluorine appear to be the chief anionic substituents.

3. My third comment is a word of caution about the use of Silverman
reagent and 2 % citric acid. Recent work at NZFMRA laboratories
has shown Silverman reagent to dissolve more P than $\frac{1}{2}$ or 1 % acitic
acid from oceanic phosphates. It is often not as effective in removing
free $CaCO_3$ either. We have also found that free $CaCO_3$ is selectively
soluble in 2 % citric acid relative to apatite. For solubility
assessments therefore I suggest that free $CaCO_3$ be removed first with
$\frac{1}{2}$ % acetic acid, if comparisons are to be made about reactivity,
and, also it appears, agronomic effect, with the phosphates studied
at our Otara Research Station. Others, here, may have similar and
more extensive experience of these effects.

M. HEGNER

I would like to thank Mr. Rogers for his remarks but I am afraid I am
not quite able to answer all the questions. This is a problem that we are
just starting and now working with this field, so we know how many
questions are still open and we are doing our best to study something
but we are not able to do everything. So to the first remark of course
we know the origin of the phosphates we studied but we were asked not
to disclose the results. The second question, as we know, there are
some difficulties with the analysis of phosphate; we have studied this
problem for some time and we want to have precise data but still I am
sorry we don't have it. We published all we have and there are many
problems you can see only in our paper you mentioned. Then the last
question : there was some suggestion and I agreed and I am very glad that
I can hear we can get more samples because we are interested to have
the possibility to check the properties of other phosphates. The last
question was about the meaning of the analysis using citric acid and
Silverman reagent. So in this field we have no results of our own
and took simply the data coming from literature and I am sorry I can't
comment this particular issue.

M. NIELSSON (I.M.C, U.S.A.)

My company is one of the producers of Florida rock and the only place we sell calcined rock to Japan and I was over there on a trouble shooting mission one day. The customer wanted rock no lower in CO_2 than 0.6 %. Normally we calcine at 1 000°C and we reach that level. Inadvertently the shipment that the customer received was 0.2 % CO_2 and they said that the rock was completely non reactive, that in these hemihydrate-dihydrate processes that the Japanese used generally they had to actually heat the sulphuric acid in order to get any reactivity. So we discussed it and apparently they discovered that there was certain CO_2 levels as large as 0.5. You get CO_2 coming out and the rock bounces around in the reactor and mixes. When you get down below that level, the rock becomes completely inert almost, there is no CO_2 evolution and the rock sits down at the bottom of the reactor and you get no mixing. My question is : because you can get any CO_2 you want for any degree of calcination depending upon the rock, have you any data indicating what is the lowest CO_2 level which was given good extraction in a sulphuric acid system?

M. HEGNER

I am sorry but I explained that our studies were in the way of modelling in laboratory conditions and therefore we can have from these results no recommendations for plant scale production; I hope we can succeed later.

M. KABIL (Donauchemie, Austria)

On the question of the citric acid, I would like to ask a question. Following our own work we would find that the solubility of different rocks in 2 % citric acid could be increased by successive dilution, e.g. that when we reached a 9 - 10 % solubility in the so-called hard phosphates, if we dissolved the residue of the first elution, the solubility was again slightly less than 9 %, from which we concluded that the normal solubility methods only achieve a gradual dissolution. What are your own results in that respect?

M. JEMAA (S.I.A.P.E. Tunisia)

To stay in the field of mathematical models, I would like to refer to the modelization of the crystallization of calcium sulphate in a single tank. Attempts have been made in the U.S. by RONDOLF and LASSOV to establish a model for the crystallization of calcium sulphate, but it was not possible to do it from solid products, e.g. from phosphate rock, but only from liquid monocalcium phosphate. There is a very interesting approach to this, a statistical approach, which considers the calcium sulphate population as an entity with a rate of natality and a rate of mortality. We know how to calculate the rate of natality, which is the rate of crystal nucleation; the rate of growth of the population is the rate of growth of the crystals. There remains the rate of mortality. My question is then : did you try to establish not a rate of reaction during phosphate dissolution but some kind of cinetics of phosphate

dissolution in various acids?

M. HEGNER

The answer is yes. We have the intertion of studying the cinetics of
the process, but we felt at the beginning of our work that we needed
the data we presented here to start this work and therefore we are
not able to speak today about the cinetics of the process but it is
the logical continuation of our work now. We just started it.

M. QUINTON (Fisons, U.K.)

I must first congratulate the authors on the extent of investigations.
In fact, in many points, or in samples, this confirmed what we made
at Levington several years ago. With respect to the query by Mr. Rogers
of New-Zealand we have no experience in the use of Silverman reagent.
Now I have a specific question and this refers to the measurement of
surface area and I would like to ask the authors if they have any
observations on the desirability of using a surface area exposed to
liquid rather than gas in the determination of the surface area of
the rock particle.

M. HEGNER

In our method, as we wrote in the paper, we use the BET method and
therefore we are quite familiar with this method which is used very
frequently and for this purpose I think where we would like to know
the correlation between different types of phosphates so it can be only
the relative value of the results of this measurement we can then see
how differences are between different types. Of course, the dependence
cf the exact value depends of the method you use, but we tried only this
one because we have it in our Institute.

M. PENG (C.R.A., Brazil)

I understand of course your work is related to the chemical reactivity
and we understand that there is correlation between the agronomic
reactivity and the physico chemical properties. I am just wondering
if your Institute has any plans to go into that part of the research
that is the correlation between the agronomic reactivity and the
physico chemical properties, in addition to the chemical reactivity.

M. HEGNER

I am sorry this is not exact, we have never tried to confirm the agronomic
characteristics and value of different types of phosphates because we
don't use much rock phosphate as such in Czechoslovakia but we want to go
from this practice to a better fertilizing of course. So it is not our
concern or intention to evaluate the agronomic characteristics and the
value of different types of phosphates.