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**In 1982, the name of the International Superphosphate Manufacturers' Associations (ISMA) was changed to International Fertilizer Industry Association (IFA).*

CAKING AND DEGRADATION OF GRANULAR COMPOUND FERTILIZERS
CONTAINING NITRATES AND SULFATES

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Introduction

Large amounts of granular compound fertilizers containing nitrates and sulfates have been produced in Europe and also in Japan, U.S.A., and other countries. Some of the products often cake seriously in storage while others degrade into powder, but the reason for these changes has not been clear. The author has tested compound fertilizers produced in European countries and has found that both the caking and the degradation can be caused by the formation of a double salt $(\text{NH}_4, \text{K})(\text{NO}_3)_2\text{SO}_4$ ("B"). Phase diagrams of the systems $\text{NH}_4\text{NO}_3 - (\text{NH}_4)_2\text{SO}_4$, $\text{NH}_4\text{NO}_3 - \text{KNO}_3$, and $\text{NH}_4\text{NO}_3 - \text{KNO}_3 - \text{K}_2\text{SO}_4 - (\text{NH}_4)_2\text{SO}_4$ were prepared and volume change and heat of the phase changes were studied as a fundamental research for the caking and degradation.

Granular compound fertilizers tested

Three commercial products of granular compound fertilizers, S-1 (20-11-11), F-1 (15-20-15), and T-1 (16-16-16) were tested. S-1 and F-1 were made with ammoniated slurry of wet-process phosphoric acid, potassium chloride, and ammonium nitrate and sulfate by granulation at about 80° C with about 5 % moisture and drying between 80 and 100° C. S-1 has a tendency to degrade into powder in storage while F-1 cakes considerably. T-1 was granulated with powdered ammonium phosphate and potassium chloride by spraying a concentrated solution of ammonium nitrate and has a tendency to cake slowly in storage. Moisture content was 0.3 % for S-1 and 0.5 % for F-1 and T-1.

The result of X-ray quantitative analysis (1,2) of the compounds present in the products is shown in table I. The X-ray analysis was made a few weeks after the production in the factories. S-1 had partly degraded and F-1 caked while T-1 was in good shape. For S-1 and F-1, potassium chloride had entirely reacted with ammonium salts to form ammonium chloride, double salts and solid solutions. A considerable amount of potassium chloride remained in T-1.

$\text{NH}_4\text{NO}_3 - (\text{NH}_4)_2\text{SO}_4$ system

Two double salts $3\text{NH}_4\text{NO}_3 \cdot (\text{NH}_4)_2\text{SO}_4$ ("A") and $2\text{NH}_4\text{NO}_3 \cdot (\text{NH}_4)_2\text{SO}_4$ ("B") have been known to exist in this system (3) but their thermal changes have not been reported. A phase diagram made by the present author (4) is shown in figure 1.

Ammonium sulfate affected the inversion of ammonium nitrate. When more than 3 % (mole %) sulfate was present, Form III ammonium nitrate did not appear and

Form IV inverted directly into II at 51° C, while the temperature of the inversion from II to I was lowered from 125° to 107° C. Melting point was raised from 169° to 181° C by addition of 5 % sulfate.

When the sulfate exceeded 5 %, the melting point increased markedly and $(\text{NH}_4)_2\text{SO}_4$ crystallized first from the melt on cooling. On further cooling Form I NH_4NO_3 crystallized at 181° C and then "A" formed at 162° C. On heating, "A" decomposed at 162° C into NH_4NO_3 (I) and $(\text{NH}_4)_2\text{SO}_4$.

When a mixture of two moles NH_4NO_3 and one mole $(\text{NH}_4)_2\text{SO}_4$ was heated to 180° C and cooled to room temperature, the product was a mixture of "A" and $(\text{NH}_4)_2\text{SO}_4$, which reacted slowly at room temperature to form "B". The formation of "B" was accelerated by moisture. On heating, "B" did not decompose below 160° C when dry but partially decomposed into "A" and $(\text{NH}_4)_2\text{SO}_4$, even at 80° C when moisture was contained.

$\text{NH}_4\text{NO}_3 - \text{KNO}_3$ system

Coats (5) reported the phases of the system below 135° C but did not complete the phase diagram. A diagram made by the present author is shown in Figure 2. A small amount of KNO_3 stabilized form III NH_4NO_3 in a wide temperature range. At room temperature, as much as 25% of NH_4NO_3 in form III NH_4NO_3 could be replaced by K. A double salt $\text{NH}_4\text{NO}_3 \cdot 2\text{KNO}_3$ ("C") appeared when K exceeded 25%.

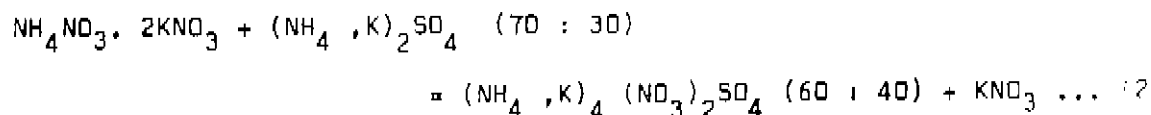
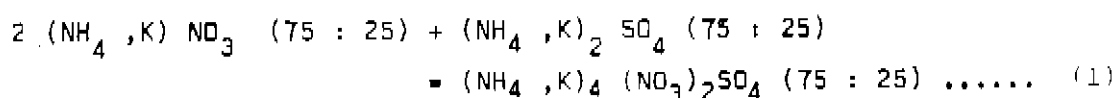
Stable forms of pure KNO_3 were II and I below and above 130° C, respectively. On cooling pure KNO_3 , form III (III' in Figure 2) temporarily appears at 126° C (6). The present tests have shown that III' and "C" are isomorphic and can form a solid solution in a wide range up to 87 moles NH_4NO_3 and 13 moles KNO_3 around 120° C. The "C" solid solution inverted into form I KNO_3 solid solution at higher temperatures. On cooling, the "C" solid solution decomposed to "C" of the stoichiometric composition and NH_4NO_3 (III) or KNO_3 (II) according to the composition of the solid solution.

$\text{NH}_4\text{NO}_3 - \text{KNO}_3 - \text{K}_2\text{SO}_4 - (\text{NH}_4)_2\text{SO}_4$ system

A phase diagram of the system based on the tests below 180° C is shown in Figure 3. Tests above 180° C did not give reliable results because of the decomposition of NH_4NO_3 . Nikonova (7) reported that a double salt $2\text{NH}_4\text{NO}_3 \cdot \text{KNO}_3$ first crystallized from a melt rich in NH_4NO_3 and KNO_3 . The present tests have shown that such double salt may not exist and that in a range $X < 0.05$ and $Y > 0.15$ a solid solution of form I KNO_3 crystallized first from the melt and then inverted into "C" solid solution which could have a chemical composition of 2 moles NH_4NO_3 and one mole KNO_3 . A continuous solid solution could be formed between $(\text{NH}_4)_2\text{SO}_4$ and K_2SO_4 (NKS). When x was larger than 0.05, melting point increased markedly and NKS crystallized first from the melt.

In other series of tests, various mixtures of the system were heated at 160° C, kept at 150° C for an hour and then cooled rapidly to room temperature, similarly to the treatments in melt granulation of compound fertilizers. Figure 4 shows the compounds present in the products immediately after the cooling. "A" was present only when Y was smaller than 0.1. When Y was larger than 0.1, "B" and form III NH_4NO_3 appeared in place of "A". Essentially no K was contained in "A" while up to 40% of NH_4 in "B" could be replaced by K.

Figure 5 shows the compounds present after the above products were moistened with about 3% water and kept at room temperature until an equilibrium was reached. Figures 4 and 5 indicate that NKS and NH_4NO_3 (III) or "C" coexisted in a wide range immediately after the cooling and that these reacted at room temperature to form "B". Two examples of the reactions are as follows :



The numbers between brackets in the equations indicate atomic ratio of NH_4 : K in the solid solutions.

Thermal change of the compounds

An example of differential thermal and high-temperature X-ray analyses is shown in Figure 6. At room temperature, the sample consisted mainly of "B" (60 : 40) with small amounts of KNO_3 (form II) and NKS. On heating, KNO_3 changed to "C" solid solution at 110° C and then to a solid solution of form I KNO_3 (I') at 130° C. At 150° C, "B" decomposed into NKS and I'. On cooling, I' changed to "C" solid solution at 130° C. The compounds present at room temperature immediately after the cooling were "C" and NKS. When the mixture of "C" and NKS was moistened and kept at room temperature, a large amount of "B" formed with a small amount of KNO_3 (form II), following the above reaction (2).

Other tests have shown that when samples containing "B" were moistened with about 5% water and heated to 80° C as in the case of granulation of compound fertilizers, a portion of "B" decomposed to form NKS and "C" or NH_4NO_3 (III). The decomposition occurred more readily when larger amount of K was contained in "B". On the other hand, the formation of "B" from NKS and "C" or NH_4NO_3 (III) at room temperature occurred more readily when less K was present.

Volume change and heat of reaction

Heat of formation of double salts and solid solutions as determined by the measurement of the heat of solution in water is shown in Table II. The formation reactions are endothermic. The heat absorption on the formation of "B" increased with K content.

Table III shows the true density of the double salts, solid solutions and the mixtures of the simple salts of the equal chemical composition. The volume increases when the double salts and the solid solutions are formed from the simple salts. The volume increase on the formation of "B" was fairly large when K was not contained and was smaller with the increasing amount of K.

Tests with commercial products rich in "B"

S-1 and F-1 contain a considerable amount of "B" being produced by slurry granulation with ammonium nitrate and sulfate. "B" in F-1 contains larger amount of K than does "B" in S-1. The samples were tested by X-ray a few weeks after the production, and therefore, it is possible that some changes had occurred during the few weeks. In order to find the phases present immediately after the production, S-1 and F-1 were moistened with 5% water, kept at 80° C for an hour in a sealed tube, dried at 80° or 100° C, cooled to room temperature, and immediately tested by X-ray. These samples are marked as S-80, S-100, F-80 and F-100 in Table I according to the drying temperature.

S-80 and F-80 contain less "B" than do S-1 and F-1 respectively. S-100 and F-100 contain even less "B". When the samples after the cooling was moistened with 1% water at room temperature, "B" increased rapidly for S-80 and S-100 and slowly for F-80 and F-100; the composition approached that of S-1 and F-1 respectively.

These results indicate that the composition of the products immediately after the production might be similar to S-80, S-100, and F-80, F-100 and changed to S-1 and F-1 in a few weeks in storage.

The heat of the formation of "B" by the above reactions was determined by the measurement of the heat of solution in water of S-1, S-80, F-1, and F-80. The test showed that 0.5 cal/g was emitted by the change from S-80 to S-1 while 0.1 cal/g absorbed by the change from F-80 to F-1. The heat agrees well with that calculated from the data of Tables I and II.

Volume change was calculated based on the data of Table III for the above mentioned reactions (1) and (2) which are similar to the changes from S-100 or S-80 to S-1 and F-100 or F-80 to F-1, respectively. The calculation showed a 3.2% volume increase for the reaction (1) and a 1.4% volume decrease for the reaction (2).

These results indicate that for S-1 "B" increased in storage with a heat emission and a considerable expansion resulting in the degradation of the granules, while for F-1 "B" increased slowly with minor heat absorption and volume decrease causing no degradation. It has been observed that the granules of F-1 have many white protuberances consisting of "B" on the surface of the granules and the protuberances combine the granules resulting in the caking. It is likely that moisture on the surface of the granules was lost during the drying step but some moisture remained inside the granules as a saturated solution which slowly diffused to the surface of the granules and formed "B" in storage.

The phosphates and chloride present in the fertilizers (Table I) did not show any appreciable effect on the changes of the nitrates and sulfates.

Change of T-1 in storage

The sample T-1 contained a considerable amount of potassium chloride while all of the chloride had reacted during the production of S-1 and F-1. It is likely that the difference is due to the different granulation process - use of powdered ammonium phosphate - which would result in less recycle ratio and lower granulation temperature. The sample was stored for one year in a sealed bottle at room temperature and then tested again by X-ra. The result is shown in Table I as T-2. In one year KCl and NH_4NO_3 reacted considerably to form NH_4Cl , "C" and KNO_3 by the following equation :



The sample showed a slight tendency to cake in storage without degradation. A calculation indicated that the volume decreases by 0.9% with the reaction (3). The sample contains less "B" and seems not to be affected appreciably by "B".

Prevention of degradation and caking

The following ways are suggested to prevent the degradation and caking :

- (a) Decreasing the amount of "B" by controlling the NO_3/SO_4 and NH_4/K ratios
- (b) The degradation may be prevented by keeping the $\text{K}/(\text{NH}_4 + \text{K})$ ratio of "B" larger than 0.3.
- (c) For the products which would contain a considerable amount of "B", the granulation and the drying should be made at lower temperature so that not much "B" is decomposed.

- (d) Moisture of the product should be kept low to delay the reactions in storage.
- (e) For the products with less "B" such as T-1, granulation at higher temperature at larger recycle ratio may be helpful to complete the reactions before the product are put in storage.

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TABLE 1 COMPOUNDS PRESENT IN FERTILIZER (%)

COMPOUNDS	<u>20 - 11 - 11</u>			<u>15 - 20 - 15</u>			<u>16 - 16 - 16</u>	
	<u>S - 1</u>	<u>S - 80</u>	<u>S - 100</u>	<u>F - 1</u>	<u>F - 80</u>	<u>F - 100</u>	<u>I - 1</u>	<u>I - 2</u>
III - (NH ₄ ,K)NO ₃	10 (75:25)	13 (75:25)	18 (75:25)	0	0	0	22 (75:25)	11 (75:25)
KNO ₃	0	0	0	3	3	0	3	10
NH ₄ NO ₃ ·2KNO ₃	13	14	16	0	6	13	10	15
(NH ₄ ,K) ₄ (NO ₃) ₂ SO ₄	39 (75:25)	32 (75:25)	20 (75:25)	23 (60:40)	12 (60:40)	5 (60:40)	5 (70:30)	6 (60:40)
(NH ₄ ,K) ₂ SO ₄	0	3 (75:25)	8 (75:25)	13 (30:70)	20 (40:60)	23(50:50)	1 (30:70)	0
KCl	0	0	0	0	0	0	10	4
NH ₄ Cl	14	14	14	21	21	21	16	21
(NH ₄ ,K)H ₂ PO ₄	17 (95: 5)	17 (95: 5)	18 (95: 5)	23 (95: 5)	24 (95 :5)	25(95: 5)	23 (95 : 5)	23 (95: 5)
(NH ₄) ₂ HPO ₄	1	1	0	9	8	7	0	0

Numbers between brackets indicate NH₄ : K ratio of solid solutions

TABLE II HEAT OF FORMATION OF DOUBLE SALTS AND SOLID SOLUTIONS

FROM SIMPLE SALTS (25° C)

COMPOUNDS	ΔH (Kcal/mole)	ΔH (Cal/g)
$3 \text{ NH}_4 \text{ NO}_3 \cdot (\text{NH}_4)_2 \text{ SO}_4$	1.64	4.4
$(\text{NH}_4, \text{K})_4 (\text{NO}_3)_2 \text{ SO}_4$ (100: 0)	0.75	2.2
$(\text{NH}_4, \text{K})_4 (\text{NO}_3)_2 \text{ SO}_4$ (75 :25)	1.75	6.2
$(\text{NH}_4, \text{K})_4 (\text{NO}_3)_2 \text{ SO}_4$ (65 :35)	2.73	8.5
$\text{NH}_4 \text{ NO}_3 \cdot 2 \text{ KNO}_3$	2.42	8.6
$(\text{NH}_4, \text{K})_2 \text{ SO}_4$ (50 :50)	0.65	4.2
III - $(\text{NH}_4, \text{K}) \text{ NO}_3$ (75 :25)	0.27	3.1

Numbers between brackets indicate NH_4 : K ratio of solid solutions

TABLE III DENSITY OF DOUBLE SALTS AND SOLID SOLUTIONS AND

EXPANSION ON THEIR FORMATION

COMPOUNDS	DENSITY ^(a)	DENSITY ^(b)	EXPANSION (%)
$3 \text{ NH}_4 \text{ NO}_3 \cdot (\text{NH}_4)_2 \text{ SO}_4$	1.702	1.759	3.35
$(\text{NH}_4, \text{K})_4 (\text{NO}_3)_2 \text{ SO}_4$ (100: 0)	1.691	1.764	4.32
$(\text{NH}_4, \text{K})_4 (\text{NO}_3)_2 \text{ SO}_4$ (75 :25)	1.833	1.874	2.24
$(\text{NH}_4, \text{K})_4 (\text{NO}_3)_2 \text{ SO}_4$ (65 :35)	1.904	1.918	0.74
$\text{NH}_4 \text{ NO}_3 \cdot 2 \text{ KNO}_3$	1.918	2.000	4.28
$(\text{NH}_4, \text{K})_2 \text{ SO}_4$ (50 : 50)	2.171	2.205	1.57
III - $(\text{NH}_4, \text{K}) \text{ NO}_3$ (75 :25)	1.821	1.858	1.98

Density of double salts and solid solutions (g/ml)

Density of mixtures of simple salts (g/ml)

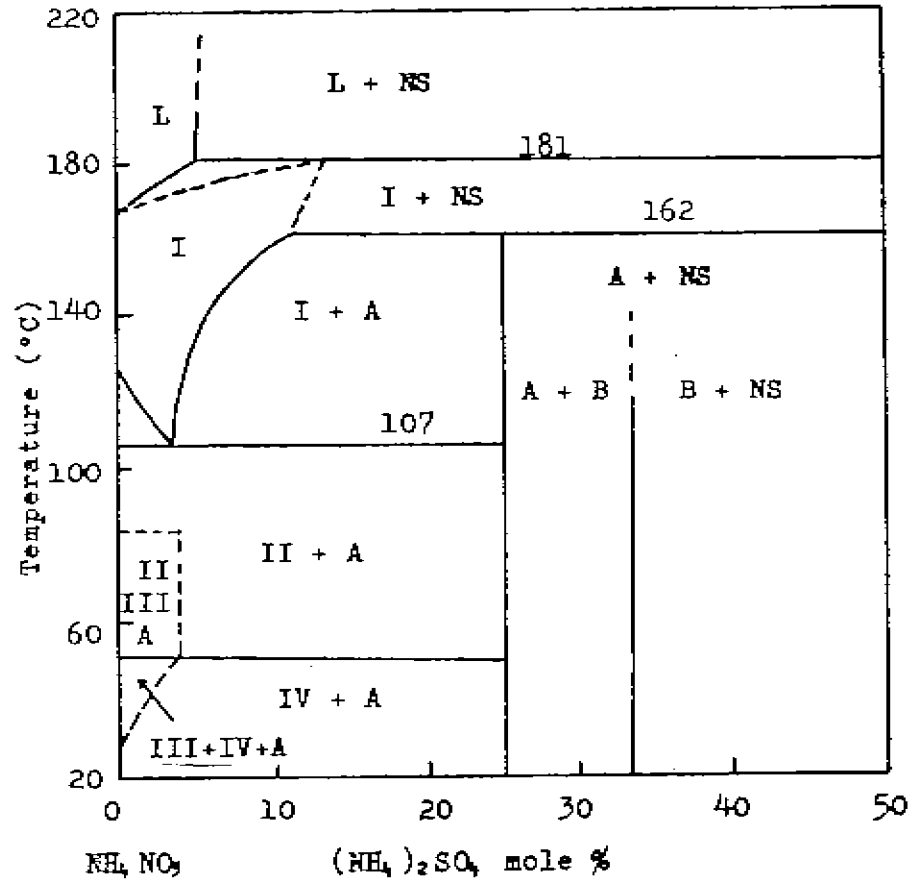


FIGURE 1 PHASE DIAGRAM OF NH_4NO_3 - $(\text{NH}_4)_2\text{SO}_4$ SYSTEM

I: FORM I NH_4NO_3 A: $3\text{NH}_4\text{NO}_3 \cdot (\text{NH}_4)_2\text{SO}_4$
 II: FORM II NH_4NO_3 B: $2\text{NH}_4\text{NO}_3 \cdot (\text{NH}_4)_2\text{SO}_4$
 III: FORM III NH_4NO_3 L: LIQUID
 IV: FORM IV NH_4NO_3 NS: $(\text{NH}_4)_2\text{SO}_4$

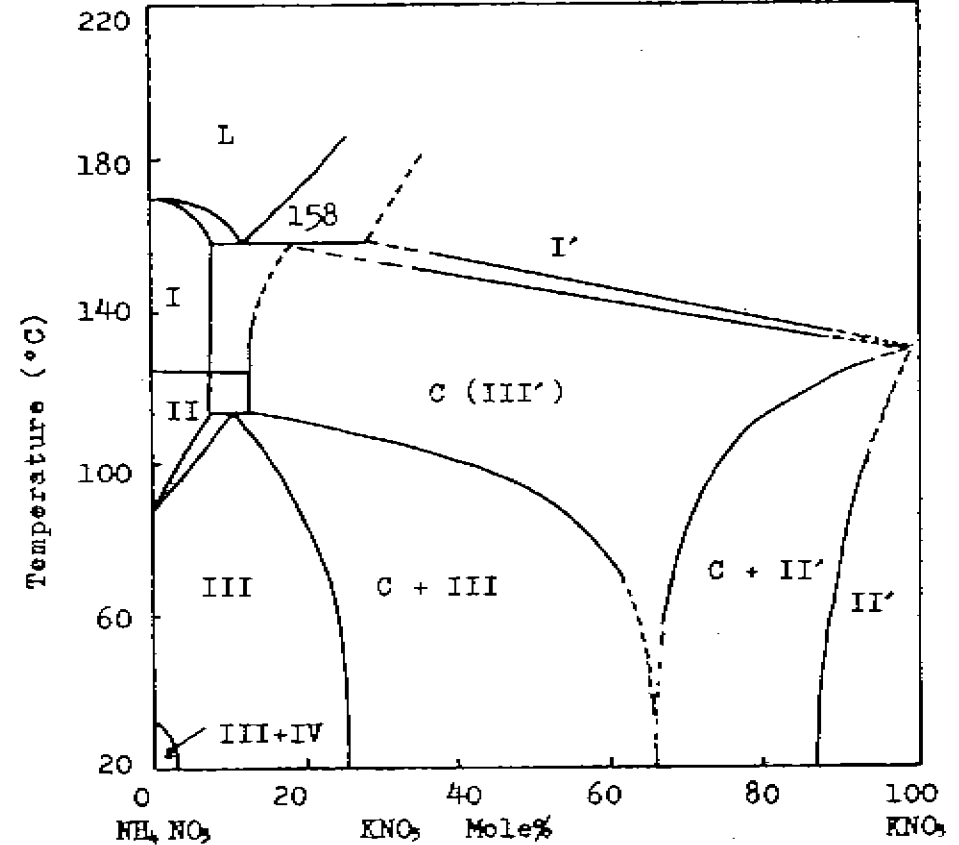


FIGURE 2 PHASE DIAGRAM OF NH_4NO_3 - KNO_3 SYSTEM

I' : FORM I KNO_3 III' : FORM III KNO_3
 II' : FORM II KNO_3 C : $\text{NH}_4\text{NO}_3 \cdot 2\text{KNO}_3$

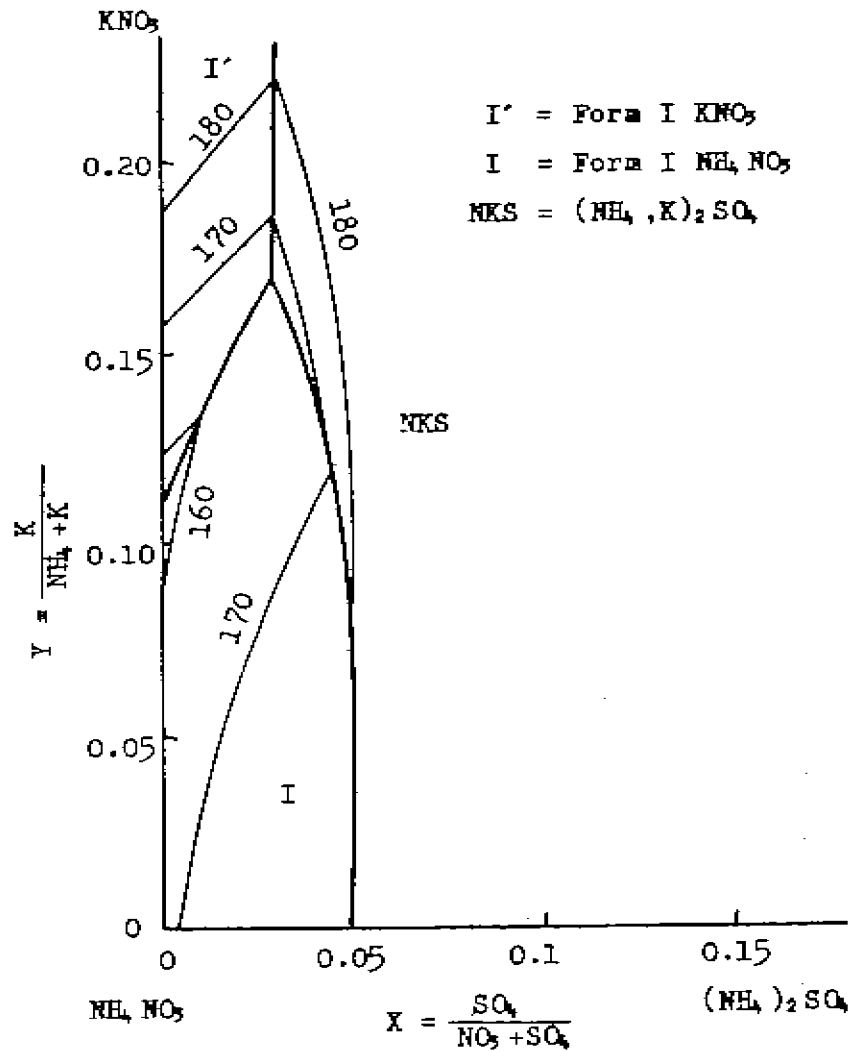


FIGURE 3 PHASE DIAGRAM OF $NH_4NO_3 - KNO_3 - K_2SO_4 - (NH_4)_2SO_4$ SYSTEM

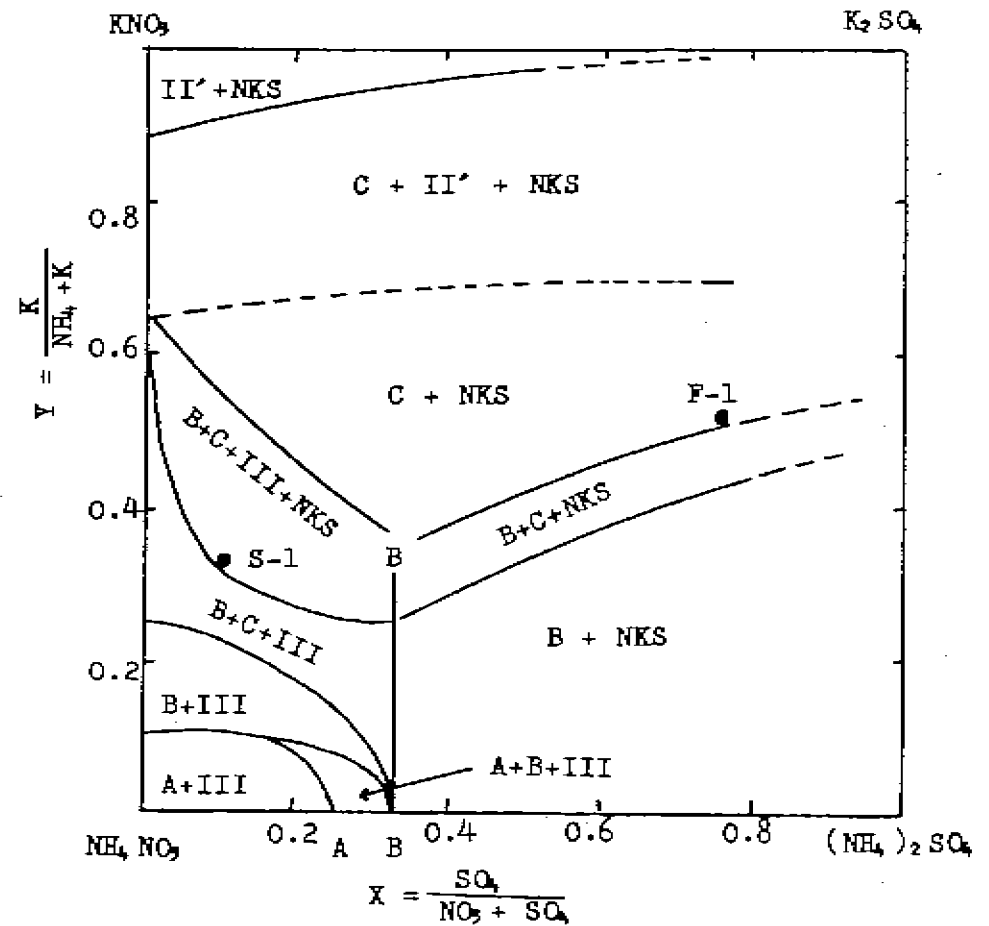


FIGURE 4 COMPOUNDS IMMEDIATELY AFTER COOLING TO ROOM TEMPERATURE FROM $150^\circ C$

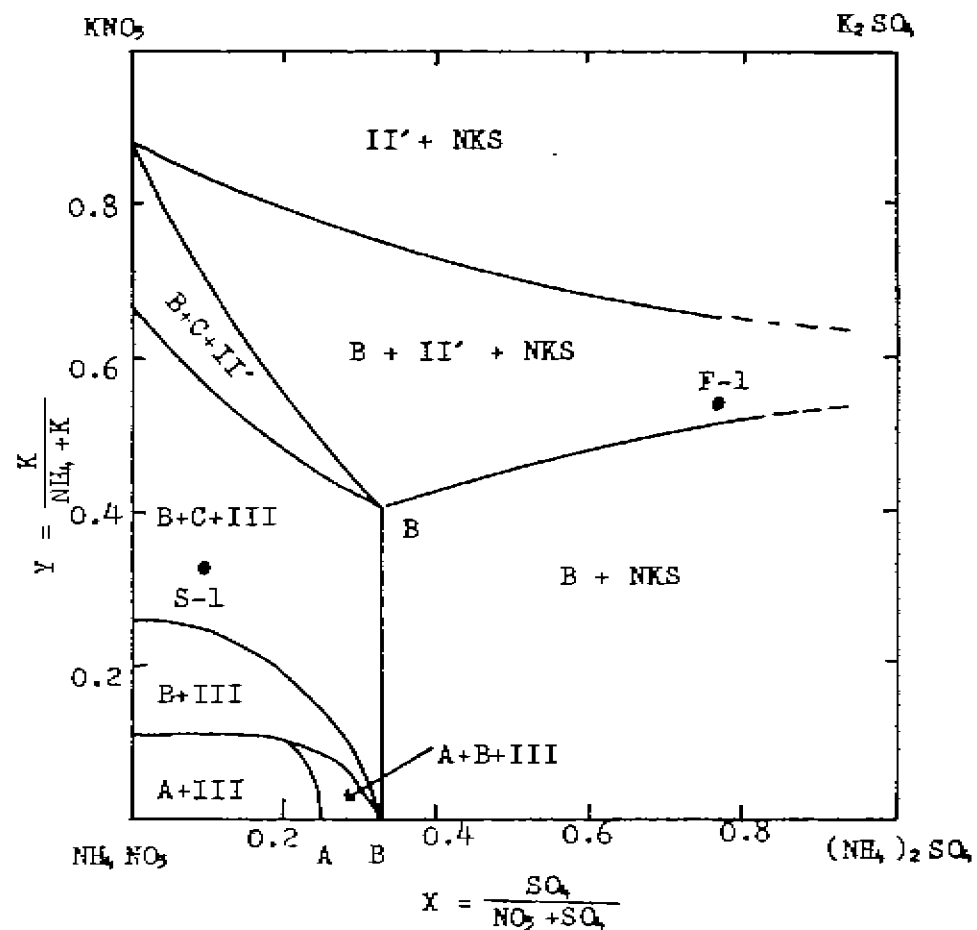
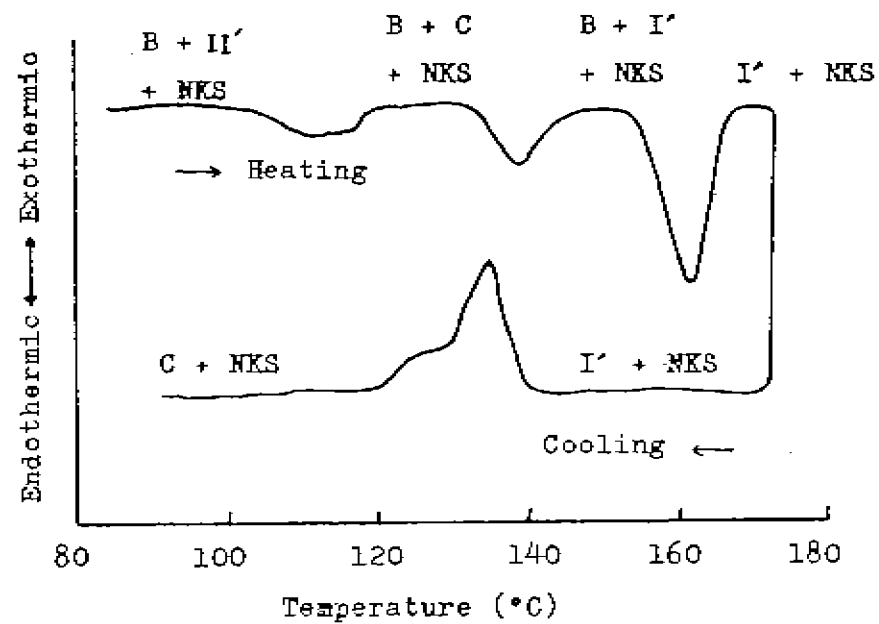


FIGURE 5 COMPOUNDS STABLE AT ROOM TEMPERATURE

FIGURE 6 DTA CURVE OF A SAMPLE $X=0.33, Y=0.5$
(I' means I-KN)

DISCUSSIONProf. J. ANDO (Chuo University, Japan)

My presentation today deals with caking and degradation of compound fertilizers and I think this caking is a very common problem throughout the world. On page 7 of my paper, table 1 shows 3 samples of compound fertilizers sent from different European countries to my laboratory. Caking can occur if any new phase is formed between granules. If this new phase is very hard, the caking is hard, and if the formation of new phases occurs in the granule itself and causes expansion, the granule can degrade into powder. In this table the 16-16-16 sample made from solid ammonium phosphate and potassium chloride, on which ammonium nitrate solution was sprayed, and granulated, the reaction does not proceed completely during the granulation process. It is shown here that T-1 -this is the product very soon after the production- contains very large amounts of unreacted potassium chloride, about 10%, remains. T-2 is the same product tested about 1 year after it is stored and it shows that the potassium chloride content decreased to 4% and ammonium chloride increased and ammonium nitrate-potassium nitrate double salts increased. This reaction can cause caking. So for these samples the good thing is to finish up the reaction during the granulation and cooling steps; for this purpose the finer grinding of potassium chloride will finally promote the reaction and also the use of large amount of recycle also promotes the chemical reaction. And the other two samples 20-11-11 and 15-20-15 were made with ammonium phosphate slurry, ammoniated wet process phosphoric acid, with potash, ammonium sulfate and so on and they use large amounts of recycle. So the reaction is essentially complete during the granulation. So for those samples S-1 and F-1 respectively are the products just after the production and so KCl is all gone; no KCl is included and so this shows the reaction is almost complete during the granulation stage. Still this 20-11-11 degrades very badly into powder during storage and 15-20-15 cakes very badly during storage. So some different chemical reactions occur during storage and this is caused by the temperature difference. The granulation takes place at about 80°C, drying at about 100°C and then it is cooled and stored phases present at high temperature and low temperature are different. That is shown in Figure 1 page 9. There are 2 figures shown here and those phases present differences with temperature. So owing to the temperature difference the reaction can occur and this causes the problem. In this present study the most important compound I found which causes the early degradation and caking -table 1 again- is the compound double salt of ammonium potassium nitrate sulphate we called B $(\text{NH}_4\text{K})_4(\text{NO}_3)_2\text{SO}_4$ and for example for 20-11-11 S-80 shows the phase at 80° during the granulation process and F-100 shows phases at 100°C, possibly the drying step, so the amount of this compound varies from 39 to 20 and after it is cooled at room temperature gradually again this compound increases and the formation of this compound also accompanied with a volume change and a thermal change. The same things happened for the 15-20-15 the amount of this compound is different at room temperature, 80° and 100°.

1st slide

This compound is very important in Japan and this shows expansion at the formation of these compounds and this shows various ratios ammonium/potash in the compound and expansion differs. Expansion is very substantial when less potash is present, less expansion when much potash is present. So when such a high ammonium double salt forms, much expansion occurs and it can cause the degradation of a granule as in the case of 20-11-11. However for other product 15-20-15 this expansion is rather low when the soluble salts solution reacts. I found this. In that case a volume decrease can easily occur. So I think this is a very important compound.

Next slide

This shows a thermal change. The formation of all these compounds is an endothermic reaction.

Mr. HUIJGEN (U.K.F., Netherlands)

The phenomenon of caking is as old as the fertilizer industry, and one could have hoped that the subject had disappeared from fertilizer research programs long ago. It probably has been the most expensive research item in the fertilizer industry, because it is still on the list with many companies.

And fertilizers still cake, although, it must be said at increasingly higher levels of product quality.

One of the difficult points about caking is that one should not generalize. What is good for one formulation, manufactured in a certain process, should not necessarily apply to different compositions or to products made by a different process.

At first sight therefore it seems impossible to arrive at conclusions by studying only three products S-I, F-I, and T-I (I refer to page 1 of the paper), because there are differences not only in formula, but also in process, in mole ratio $\text{NH}_3/\text{H}_3\text{PO}_4$ and in moisture content.

However Prof. ANDO's approach is rather fundamental and I think his theory and experiments explain the behaviour of the three grades mentioned rather well.

The main lesson we have to learn from the paper is the volume increase when the "B" material, 2 nitrate, one sulfate, is formed. Either degradation or caking results from this formation.

Some of our own experience may be explained by Prof. ANDO's work. A formulation 25-5-5 based on potassium sulphate was very difficult to granulate in our normal system because of the high plasticity of the material. In this system drying was indeed done at temperatures higher than advised in your paper.

We do not think that degradation results from one phase change, but that more numerous changes have to occur.

May I finish by asking the following questions :

1. At which figure of moisture percentage did phase III not appear in your experiments with nitrate and sulfate ?
2. Could you comment on the behaviour during granulation in the light of the plasticity of the material ?
3. In figures 4 and 5 you defined x as $\frac{SO_4}{NO_3 + SO_4}$. Did you consider to use equivalents rather than moles, so that possibly the lines could become straight ?

Prof. ANDO

I think your first question is related to the moisture content and the presence of the form III ammonium nitrate.

Slide N°4

It shows that for pure ammonium nitrate the moisture content is normally about less than 1%. Form III disappears. Also it helps this form to disappear even when the moisture content is over than 0.1% When very large amounts of sulphate is present form III did not appear.

On this slide I would like to mention something about plasticity. Plasticity results from two things. The main one is the ratio of the amount of liquid phase and solid phase and naturally when the ammonium nitrate is high the melting point is low.

Concerning the form III of ammonium nitrate, figure 2 of my paper, page 9 here, form III is stabilized by the presence of potash. So even when there is no moisture form III is always present at a very high temperature range. So I just mention that the presence of this form III is affected very much by potash and sulphate and also by moisture.

Concerning the 2nd question on plasticity the lower melting point of the ammonium nitrate potassium nitrate system represents about 10% potassium nitrate, the temperature 155°C. Actually the compound fertiliser contains phosphate, some moisture. So even at 60° or 80° very large amounts of the liquid phase can be present in the phase. The amount of liquid phase is most important for the plasticity and another thing is the plasticity of the solid material itself which means when ammonium nitrate is a high temperature, solid material can itself be very plastic. So I think the plasticity is really the two things.

About the 3rd question on page 10 and here, two black points show S-1 and F-1 and in this range the expansion occurs by the formation of this compound "B", so this figure 4 represents the phase just after this could form at 100 to 50°C. It corresponds to the product just after prilling and after it is stored at room temperature; the phase is gradually changed to figure 5, page 11. Figure 5 is the stable phase at room temperature. So there is a large difference in the phases and by the formation of this compound B double salt in the S-1 which contains less ammonia the formation of B causes expansion, and F-1 corresponds to another sample high in potash. In this case expansion does not occur. So by changing the formulation, we can control the amount of expansion or the caking and so on, and I agree with Mr. Huigjen's view that caking and degradation can be caused by many reactions not only one simple reaction. It is perfectly true but for degradation, the expansion is necessary, otherwise any change which does not cause expansion and does not cause degradation. So I think the formation of compound B high in ammonia may be the origin of the degradation.

Mr. MELINE (T.V.A., U.S.A.)

Have you included in your studies compounds containing polyphosphates and, if so, why do they have such good storage properties?

Prof. ANDO

No, but any phosphate fertilizer prilled can contain some polyphosphate, 10% or 15%, just because owing to high temperature some of them are polymerized. Even in the rotary drum granulator dryings done at 100° then 5-10% of phosphate can be polymerized.

Mr. MELINE

We do find that polyphosphate does improve storage quality very much.

Mr. SCARTAZZINI (Cdf Chimie, France)

I would like to ask Professor ANDO by which method he determined the density of his products?

Prof. ANDO

I use the specific gravity vessel. I put the oil into it and the fine material and measure the density of the simple salts and the double salts.

Mr. DAVIS (T.V.A., U.S.A.)

I noticed that your studies were made with formulations based on nitrates. Urea is increasing in importance in the world. I wondered if you might have made similar studies based on urea and if you could speculate as to whether or not you might see similar severe expansion effect and the comparative tendency to cake if urea were used instead of ammonium nitrate.

Prof. ANDO

I have also tested compounds containing urea and of course caking occurred very severely with the compound containing much urea, but I have no experience on the degradation of urea based compound. The reason why I presented the paper on nitrate is that I think in Western and Eastern Europe you are using much nitrate based compounds.