Caking And Degradation Problem on Nitrogenous Fertiliser and Alternative Solution Processes

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Received: January 20, 2011 Accepted: February 14, 2011 doi:10.5539/ijc.v3n3p123

Abstract

Toward the end of the 1950s, the development of new techniques to improve the yields from available agricultural areas has become essential to meet food requirements owing to the rapidly increasing world population. Therefore, new strategies have been determined to increase product quality in industries that serve agricultural areas.

In this study, we attempted to minimise unwanted reactions involved in the manufacturing process of chemical fertilisers.

Keywords: Nitrogenous fertilisers, Caking problem, Degradation problem, Double salts

1. Introduction

Most of the granular and prilled fertiliser that contains sulphates and nitrates is produced in Europe, Japan, and the USA. After production, some of these products degrade whereas other products suffer caking problems. In this study, prilled fertiliser that has been produced in Turkey was tested and the causes of caking and degradation problems in $(NH_4,Mg)_4(NO_3)_2SO_4$ double salts, called B, were determined. NH_4NO_3-$(NH_4)_2SO_4$, NH_4NO_3-$Mg(NO_3)_2$ and NH_4NO_3-$Mg(NO_3)_2$-$MgSO_4$-$(NH_4)_2SO_4$ solutions were prepared and the phase change and volume change in heat were analysed as the main focus area for the caking and degradation problem.

2. Testing of prilled fertilisers

Previous studies have revealed that 26% nitrogenous fertiliser (CAN-calcium ammonium nitrate), 33% nitrogenous fertiliser (AN-ammonium nitrate) and 35% nitrogenous fertiliser (AN-$Mg(NO_3)_2$) are used most often in the manufacture of nitrogenous fertiliser. Furthermore, 26% nitrogenous fertiliser (CAN) and 33% nitrogenous fertiliser (AN) have been produced by prilling: drying at 100 ℃; reacting at 170 ℃ with 0.3% moisture; followed by the addition of HNO_3, NH_3, and $CaCO_3$ (Ando, Siegal & Jordan, 1965, pp. 13). The 26% nitrogenous fertiliser tends to cake whereas 33% nitrogenous fertiliser tends to degrade (Ando, Miyamura & Akiyama, 1967). In addition 35% AN is made by mixing ammonium nitrate and magnesium nitrate ($Mg(NO_3)_2$) and prilling the solution. This product tends to degrade slowly when stored (Ando & Sai, 1970, pp. 2614). The 26% CAN contains 0.3% moisture whereas the 33% AN and magnesium nitrate ($Mg(NO_3)_2$) contain 0.5% moisture. Here, determinations of the whole chemical compounds that result from the reactions were conducted using a Shimadzu GC-MS, model of a QP 5050A mass spectrometer.

X ray results of tested fertilisers are shown in Table 1. X-ray analyses were conducted using "Fischer Instruments GmbH, 2002" X-ray equipment. X-ray analyses were conducted a few weeks after production.

2.1 Ammonium nitrate- Ammonium sulphate system in the manufacture of nitrogenous fertiliser

Previous studies have indicated that there are two double salts, $3NH_4NO_3 \cdot (NH_4)_2SO_4$ (A) and $2NH_4NO_3 \cdot (NH_4)_2SO_2$ (B), present in this system (Theoret, A., & Sandorfy., 1963, pp. 57-61). However, this does

account for the thermal change of this system. In this paper, Figure 6 shows a phase diagram related to this system.

H_2SO_4 is used in the production of nitrogenous fertiliser to effectively change ammonium nitrate. If the amount of SO_4 exceeds 0.3%, ammonium nitrate (III) (orthorhombic) will not form. Therefore, ammonium nitrate (IV)(ortorhombic) is formed at 51 ℃. The temperature required to change it from form II (tetragonal) to form I (cubic) decreases from 125 ℃ to 107 ℃. The melting point of ammonium nitrate increases from 169 ℃ to 181 ℃ upon the addition of 0.5% H_2SO_4.

If the amount of H_2SO_4 exceeds 0.5%, the melting point increases markedly (Coats & Woodard, 1965, pp. 2135). Therefore, ammonium sulphate first crystallises from the solution upon cooling (Yanagi, 1965, pp. 1351). After further cooling, form I (cubic) crystallised at 181 ℃ (Levin, 1969, pp. 264). The solution contained $3NH_4NO_3.(NH_4)_2SO_4$ (A) at 162 ℃.

When the mixture of AN and H_2SO_4 was heated, the product formed was a solution of $3NH_4NO_3\cdot(NH_4)_2SO_4$ (A) and $(NH_4)_2SO_4$. When this solution cooled to room temperature, it changed to $2NH_4NO_3\cdot(NH_4)_2SO_2$ (B). The presence of moisture accelerates this reaction. When $2NH_4NO_3\cdot(NH_4)_2SO_2$ (B) is heated to 160 ℃, it decomposes into $3NH_4NO_3\cdot(NH_4)_2SO_4$ (A) and $(NH_4)_2SO_4$, its constituent molecules. This decomposition is also observed if the moisture content is low.

2.2 NH_4NO_3- $Mg(NO_3)_2$ system

The phase diagram for this system is shown in Figure 7. A small amount of $Mg(NO_3)_2$ has allowed form III (orthorhombic) of AN to be stable through a wide temperature range. At room temperature, a part of the 25% NH_3 in the form of AN, can replace the magnesium. $NH_4NO_3\cdot2Mg(NO_3)_2$ (C), a double salt, is formed when the amount of magnesium increases to 25%. This is shown in reaction (1).

The stabilised forms of pure $Mg(NO_3)_2$ assume form I and form II (tetragonal) below and above 130 ℃, respectively. From experiments conducted to observe the effect of temperature on the forms of $Mg(NO_3)_2$, we observed that pure $Mg(NO_3)_2$ and form III (II') of $Mg(NO_3)_2$ occur at 126 ℃ upon cooling. Using conducting tests, we demonstrated that $NH_4NO_3\cdot2Mg(NO_3)_2$ (C) and III'(orthorhombic) have similar forms. At about 120 ℃ these chemicals yield 87 moles of AN and 13 moles of $Mg(NO_3)_2$. After cooling, according to the composition of $NH_4NO_3\cdot2Mg(NO_3)_2$ (C) and solid solution, ammonium nitrate (form III-orthorhombic) and $Mg(NO_3)_2$ (II') (tetragonal) can be separated stoichiometrically.

2.3 NH_4NO_3–$Mg(NO_3)_2$–$MgSO_4$-$(NH_4)_2SO_4$ system

A phase diagram is obtained after testing the solution below 180 ℃ as shown in Figure 1. Testing above 180 ℃ has not yielded reliable results because AN degrades. Conduction tests revealed that $2NH_4NO_3\cdot Mg(NO_3)_2$ first crystallised in the melt that was rich in NH_4NO_3 and $Mg(NO_3)_2$. However, it might not be possible to obtain these salts all the time. For $X < 0.05$ and $Y > 0.15$, $Mg(NO_3)_2$ form I(I') (cubic) crystallized first in the melt and then changed to a $NH_4NO_3\cdot2Mg(NO_3)_2$ (C) solution with two moles of NH_4NO_3 and one mole of $Mg(NO_3)_2$ (reaction (2)). If the rate of X ($SO_4/NO_3 + SO_4$) is larger than 0.05, the melting point increases markedly and the first crystallised material will be (NH_4, Mg) SO_4 in the melt.

In another test, various mixtures of the system were heated to 160 ℃, kept at 150 ℃ for 1 hour, and then cooled to room temperature. A-$(NH_4)_2SO_4$ only occurred when Y ($Mg/NH_4 + Mg$) was smaller than 0.1. When the rate of ($Mg/NH_4 + Mg$) was smaller than 0.1, $2NH_4NO_3\cdot(NH_4)_2SO_2$ (B) and form III (orthorhombic) of NH_4NO_3 occurred instead of A-$(NH_4)_2SO_4$. In particular, when there was no Mg in $(NH_4)_2SO_4$, up to 40% of the NH_3 in $2NH_4NO_3\cdot(NH_4)_2SO_2$ (B) was replaced with Mg.

Figure 5 shows compounds of the above product having 0.3% moisture when the stabilised product formed. Figures 2 and 3 show that $(NH_4,Mg)SO_4$ and NH_4NO_3 (III)(orthorhombic), which occur simultaneously, or $NH_4NO_3\cdot2\ Mg(NO_3)_2$ (C) changes to $2NH_4NO_3\cdot(NH_4)_2SO_2$ (B) at room temperature.

$$2(NH_4,Mg)\ Mg(NO_3)_2\ (75{:}25) + (NH_4,\ Mg)_2SO_4\ (75{:}25) \rightarrow (NH_4,Mg)_4(NO_3)_2SO_4(75{:}25)\ldots\ldots\ldots(1)$$

$$NH_4NO_3\cdot2Mg(NO_3)_2 + (NH_4,Mg)_2SO_4 + (70{:}30) \rightarrow (NH_4,Mg)_4(NO_3)_2SO_4(60{:}40) + Mg(NO_3)_2\ldots\ldots\ldots(2)$$

The numbers in brackets indicate atomic rates of NH_4/Mg in the solid solution.

3. Thermal behaviour of compounds

X-ray results at high temperature and differential temperature are shown in Figure 4.

The sample whose thermal behaviour was analysed, $2NH_4NO_3\cdot(NH_4)_2SO_2$ (B), contains less $Mg(NO_3)_2$ (II') (tetragonal) and $(NH_4,Mg)_2SO_4$. When it was heated, $Mg(NO_3)_2$ changed to $NH_4NO_3\cdot2Mg(NO_3)_2$ (C) solid

solution at 110 ℃. Then, it changed to $Mg(NO_3)_2$ (I') (cubic) solid solution. At 150 ℃, $2NH_4NO_3(NH_4)_2SO_2$ (B) seperated into $(NH_4,Mg)_2SO_4$ and $Mg(NO_3)_2$ (I') (cubic). During cooling, form I' (cubic) of $Mg(NO_3)_2$ changed to $NH_4NO_3{\cdot}2Mg(NO_3)_2$ (C) solid solution at 130 ℃. After cooling, the compounds formed were $NH_4NO_3{\cdot}2Mg(NO_3)_2$ (C) and $(NH_4,Mg)_2SO_4$. The mixture of $(NH_4,Mg)_2SO_4$ and $NH_4NO_3{\cdot}2Mg(NO_3)_2$ (C) was moisturised and kept at room temperature.

In other tests, a part of $2NH_4NO_3{\cdot}(NH_4)_2SO_2$ (B) in samples containing $2NH_4NO_3{\cdot}(NH_4)_2SO_2$ (B) and 0.5% moisture at 80 ℃, decomposed into $(NH_4,Mg)_2SO_4$ and $NH_4NO_3{\cdot}2Mg(NO_3)_2$ (C) or form III (orthorhombic) of NH_4NO_3. Decomposition was realised more easily and quickly upon reaction of $2NH_4NO_3{\cdot}(NH_4)_2SO_2$ (B) and magnesium at high rates. On the other hand, at room temperature, in the reaction by Mg that has a low rate, the formation of $2NH_4NO_3{\cdot}(NH_4)_2SO_2$ (B) from NH_4NO_3 or $(NH_4,Mg)_2SO_4$ (C) occured more easily and quickly.

3.1 Volume change and reaction heat

Table 2 shows that heat of formation of the solid solution and double salts was determined by measuring the heat of dissolution of the water-soluble solution. The whole reaction was endothermic. Heat absorption in $2NH_4NO_3{\cdot}(NH_4)_2SO_2$ (B) increased with Mg.

Table 3 lists the true densities of the mixture of double salts, single salts, and solid solutions. A specific gravity vessel was used for measuring densities. For this purpose, oil was added into it along with the fine material, and the density of the simple salts and double salts were measured. If a solid solution or double salts are formed from the single salts, the volume of $2NH_4NO_3{\cdot}(NH_4)_2SO_2$ (B) will increase considerably, without Mg in the reaction. Therefore, the volume will decrease with an increase in the amount of Mg.

3.2 Testing of the commercial products containing $2NH_4NO_3(NH_4)_2SO_2$ (B) at high rates

The 26% CAN and 33% AN containing $2NH_4NO_3{\cdot}(NH_4)_2SO_2$ (B) double salt was produced by reacting AN and H_2SO_4 at high rates. $2NH_4NO_3(NH_4)_2SO_2$ (B) in 33% AN contains more Mg than $2NH_4NO_3{\cdot}(NH_4)_2SO_2$ (B) in 26% CAN. Samples were tested by X-ray studies a few weeks after production. During this time, changes in their chemical construction were as expected. To determine the phase formed after production, 26% and 33% AN fertiliser samples with 0.5% moisture were prepared in sealed test-tubes dried at 80-100 ℃, and they were analysed by X-ray after they were brought to room temperature. These samples were marked as 26% CAN/80, 26% CAN/100, 33% AN/80, and 33% AN/100 according to their drying temperatures.

26% CAN/80 and 26% CAN/100 contained much less $2NH_4NO_3{\cdot}(NH_4)_2SO_2$ (B) than they did prior to absorption of the moisture. During cooling, when the samples contained 1% moisture at room temperature, the amount of $2NH_4NO_3{\cdot}(NH_4)_2SO_2$ (B) in 26% CAN/80 and 33% AN/100 increased rapidly. The composition of the product formed at this condition is similar to that of 26% CAN and 33% AN before moisture was added.

These results indicate that the product is similar to 26% CAN/80, 26% CAN/100, 33% AN/80, and 33% AN/100. Hence, after a few weeks of storage, they could be changed to 26% CAN and 33% AN before moistured was added.

The heat of formation of $2NH_4NO_3{\cdot}(NH_4)_2SO_2$ (B), which was produced by the above reactions, was determined by measuring the heat of dissolution of an aqueous solution of 26% CAN, 33% AN, and 33% AN/80. As 0.1 cal/g of heat is absorbed during the change from AN/80 to AN, 0.5 cal/g of heat was emitted from the reaction of 26% CAN/80 to 26% CAN. Tests were conducted using a Gallenkamp, MMF-KM-073 model calorimeter bomb. The heat of the reactions can be calculated from the data in Tables 1 and 2.

Volume changes for the reaction that changes 26% CAN/100 or 26% CAN/80 (M) to 26% CAN (N) and 33% AN/100 or 33% AN/80 (M) to 33% AN (N) have been calculated in Table 3. The calculations show that the reaction volume increases by 3.23% for the first reaction (reaction (1)), and decreases by 1.4% for the second reaction (reaction (2)).

These results indicate a large volume change occurs with heat emission and prilled fertilisers degrade in storage to 26% AN with an increase in composition of $2NH_4NO_3{\cdot}(NH_4)_2SO_2$ (B). $2NH_4NO_3{\cdot}(NH_4)_2SO_2$ (B) on the surface of prilled AN forms a white blister (Figure 5). Moisture on the surface of the prilled fertiliser is lost on drying. However, the reduced amount of moisture changes the shape of $2NH_4NO_3{\cdot}(NH_4)_2SO_2$ (B) during storage.

3.3 Reactions of AN(ammonium nitrate) – $Mg(NO_3)_2$ in storage

The AN–$Mg(NO_3)_2$ (T3-1) sample can contain a large amount of $Mg(NO_3)_2$. If powdered $Mg(NO_3)_2$ is used, AN processes can end at low prilling temperatures and low inversion rates when the AN–$Mg(NO_3)_2$ sample is kept at room temperature in a sealed tube for one year. The results of X-ray analyses are listed in Table 1 as T3-2. $Mg(NO_3)_2$ and NH_4NO_3 react and form $NH_4NO_3{\cdot}2Mg(NO_3)_2$ (C) double salt and $Mg(NO_3)_2$.

$$Mg(NO_3)_2 + 1.6\ (NH_4,Mg)\ NO_3\ (75{:}25) \rightarrow NH_4NO_3 + 0.2(NH_4NO_3{\cdot}2Mg(NO_3)_2) + Mg(NO_3)_2 \quad \ldots\ldots\ldots (3)$$

The AN-$Mg(NO_3)_2$ sample cakes less without degrading in storage. In these calculations, it was seen that the volume decreased by 0.9% by reaction (3). The sample contained a small amount of $2NH_4NO_3{\cdot}(NH_4)_2SO_2$ (B), and it was seen that this double salt was not in interacting with the sample under storage conditions.

3.4 Preventing degradation and caking

These methods have been applied to prevent degradation and caking:

(a) Amount of $2NH_4NO_3(NH_4)_2SO_2$ (B) decreased by checking the rates of NO_3/SO_4 and NH_4/Mg.

(b) Degradation of $2NH_4NO_3{\cdot}(NH_4)_2SO_2$ (B) double salt decreased by setting the rate of $Mg/(NH_4 + Mg)$ to less than 0.3.

(c) Prilling and drying is realised at low temperatures to avoid degrading $2NH_4NO_3{\cdot}(NH_4)_2SO_2$ (B) in AN samples that contain a large amount of $2NH_4NO_3{\cdot}(NH_4)_2SO_2$ (B)

(d) The moisture rate in AN-$Mg(NO_3)_2$ should be kept low because reactions proceed slowly in storage.

(e) For products like AN-$Mg(NO_3)_2$ that contain less $2NH_4NO_3{\cdot}(NH_4)_2SO_2$ (B), high prilling temperature will help complete the reaction before the sample is stored.

4. Discussion

For prilled fertiliser and granular fertiliser, degradation and caking is the most important problem in storage conditions. In this research, 26% AN, 33% AN, and AN-$Mg(NO_3)_2$, the most commonly used fertilisers, were studied, and it was seen that in the final stored product depending on air moisture and temperature, any phase change in its structure caused caking. According to the amount of phase change, fertiliser prills adhere to each other, leading to more caking. As for the degradation problem, it is related to the increase in the unit volume of prilled fertilisers. If this increase is large, degradation will increase. Here, the AN-$Mg(NO_3)_2$ sample was manufactured by prilling after $Mg(NO_3)_2$ was sprayed with an ammonium nitrate solution. In these reactions, 10% unreacted $Mg(NO_3)_2$ was observed in the AN-$Mg(NO_3)_2$ samples. This product was stored for one year and thereafter, $Mg(NO_3)_2$ in the product decreased by 4%; as a result, it was observed that the amount of AN and AN-$Mg(NO_3)_2$ double salt increased. At this point, caking was observed in the product. Therefore, for all samples, reactions occuring on prilling and cooling condition must be complete, because this will prevent the formation of a new phase in the product. Therefore, decreasing the size of $Mg(NO_3)_2$ granules, which are used in the reaction, is essential to complete the reaction.

Prilling is completed at 100 ℃ and products can be stored at 80 ℃. Fertilisers stored at high and low temperatures differ from each other as shown in Figure 6. The phases resulting from temperature differences are also shown in Figure 6. Due to the temperature differences, the probable reaction that forms between prills reduces the storage life. The most important chemical compound that causes caking is $2NH_4NO_3{\cdot}(NH_4)_2SO_2$ (B) double salt that forms by the reaction between AN and H_2SO_4. In particular, 26% AN in the 26% AN/80 product shows that a new phase forms during prilling and drying. Similarly, a new phase forms in the product during prilling and drying at 100 ℃ as well. After prilling and drying, when cooling the product to room temperature, thermal changes and volume changes occur according to the composition of the double salts formed during storage. This results in caking and the degradation problem.

In this study, it could be seen that 1% moisture destroyed form III of AN that forms by the reaction between NO_3 and SO_4 (Figure 7).

Another phenomenon related to the caking problem is plasticity. Plasticity occurs when the rate between the amounts of solid and liquid phases and melting point of AN are high (Brusset, Leveau, Spinat, Trani & Verollet, 2002, pp.3).

It can be seen in Figure 7 that Mg stabilises form III of AN. Even if there is no moisture, form III (orthorhombic) of AN exists in high-temperature environments. Therefore, the existence of Mg, SO_4 and moisture are closely related to form III (orthorhombic). Another problem related to plasticity is the melting of the AN-$Mg(NO_3)_2$ system at low temperature (155 ℃). However, this is possible with 10% of $Mg(NO_3)_2$.

It has been shown in Figure 2 that the phases form in products between 50 ℃ and 100 ℃. This indicates the content of the product that forms during prilling, drying, and storage. The phase changes at room temperature are shown in Figure 3. As seen in the Figure 3, large volume differences between the phases causes caking. Therefore, if the formation of $2NH_4NO_3{\cdot}(NH_4)_2SO_2$ (B) is prevented to form by the abovementioned methods, caking and degradation problems can be solved.

5. Conclusion

At first glance, this research about nitrogenous fertilisers indicates that solutions to the caking and degradation problems cannot be generalised for all fertilisers. This is because this problem is not dependent only on formulation differences, but also on the process that is used and moisture differences in the contents. We would like to emphasise that the increase in volume that occurs during the reaction between NO_3 and SO_4 forms a $2NH_4NO_3{\cdot}(NH_4)_2SO_2$ (B) double salt. Caking and degradation problems have been derived from this formulation.

Acknowledgements

Ahmet Ozan Gezeman is thankful to his elder sister "Aysun Gezerman Dilmen" for her inspiration.

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Table 1. Compounds Present Fertiliser (%)

	26 % AN (T1)			33 % AN(T2)			35% AN-$Mg(NO_3)_2$(T3)	
Compounds	T1	T1/80	T/100	T2	T2/80	T2/100	T3-1	T3-2
III-$(NH_4,Mg)NO_3$	10(75:25)	13(75:25)	10(75:25)	0	0	0	22(75:25)	11(75:25)
$Mg(NO_3)_2$	0	0	0	3	3	0	3	10
$NH_4NO_3{\cdot}2Mg(NO_3)_2$	13	14	16	0	6	13	10	15
$(NH_4,Mg)_4(NO_3)_2SO_4$	39(75:25)	32(75:25)	20(75:25)	23(60:40)	12(60:40)	5(60:40)	5(70:30)	6(60:40)
$(NH_4,Mg)_2SO_4$	0	3(75:25)	8(75:25)	13(30:70)	20(40:60)	23(50:50)	1(30:70)	0

Numbers between brackets indicate NH_4:Mg ratio of solid solutions.

Table 2. Heat of Formation of Double Salts and Solid Solutions from Simple Salts (25 ℃)

Compounds	ΔH(kcal/mol)	ΔH(cal/g)
$3NH_4NO_3(NH_4)_2SO_4$	1.64	4.4
$(NH_4,Mg)_4(NO_3)_2SO_4$(100:0)	0.75	2.2
$(NH_4,Mg)_4(NO_3)_2SO_4$(75:25)	1.75	6.2
$(NH_4,Mg)_4(NO_3)_2SO_4$(65:35)	2.73	8.5
$NH_4NO_3{\cdot}2Mg(NO_3)_2$	2.42	8.6
$(NH_4,Mg)_2SO_4$(50:50)	0.65	4.2
III-$(NH_4,Mg)NO_3$(75:25)	0.27	3.1

Numbers between brackets indicate NH_4:Mg ratio of solid solutions.

Table 3. Density of Double Salts and Solid Solutions and Expansion on Their Formation

Compounds	Density (M)	Density (N)	Expansion (%)
$3NH_4NO_3(NH_4)_2SO_4$	1.702	1.759	3.35
$(NH_4,Mg)_4(NO_3)_2SO_4$(100:0)	1.691	1.764	4.32
$(NH_4,Mg)_4(NO_3)_2SO_4$(75:25)	1.833	1.874	2.24
$(NH_4,Mg)_4(NO_3)_2SO_4$(65:35)	1.904	1.918	0.74
$NH_4NO_3{\cdot}2Mg(NO_3)_2$	1.918	2.000	4.28
$(NH_4,Mg)_2SO_4$(50:50)	2.171	2.205	1.57
III-$(NH_4,Mg)NO_3$(75:25)	1.821	1.858	1.98

Density of soluble salts and solid solutions (g/mL)

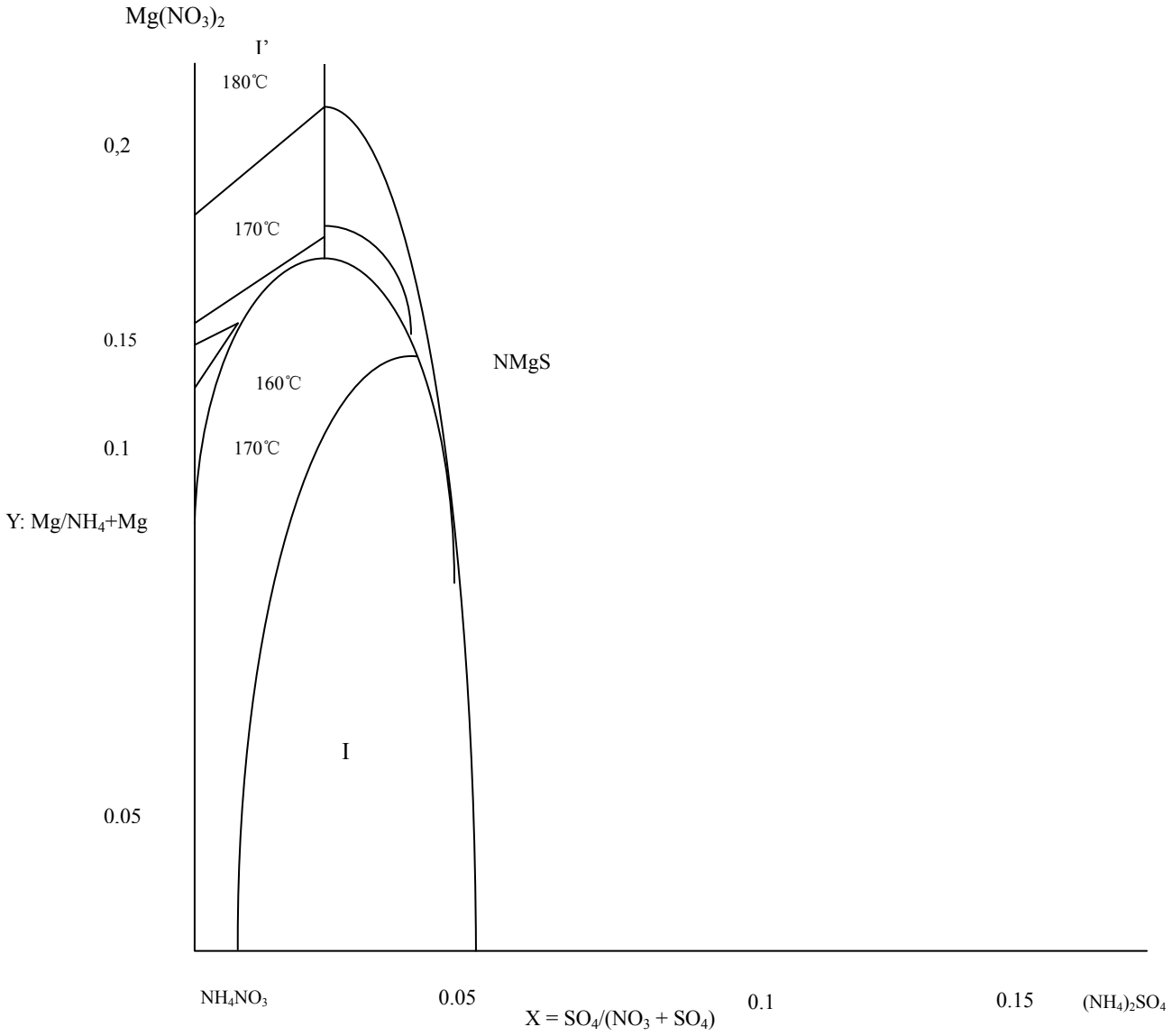


Figure 1. Phase Diagram of NH_4NO_3-$MgNO_3$-$MgSO_4$-$(NH_4)_2SO_4$ System

I': Form I $Mg(NO_3)_2$

I: Form I NH_4NO_3

NMgS: $(NH_4$: Mg) SO_4

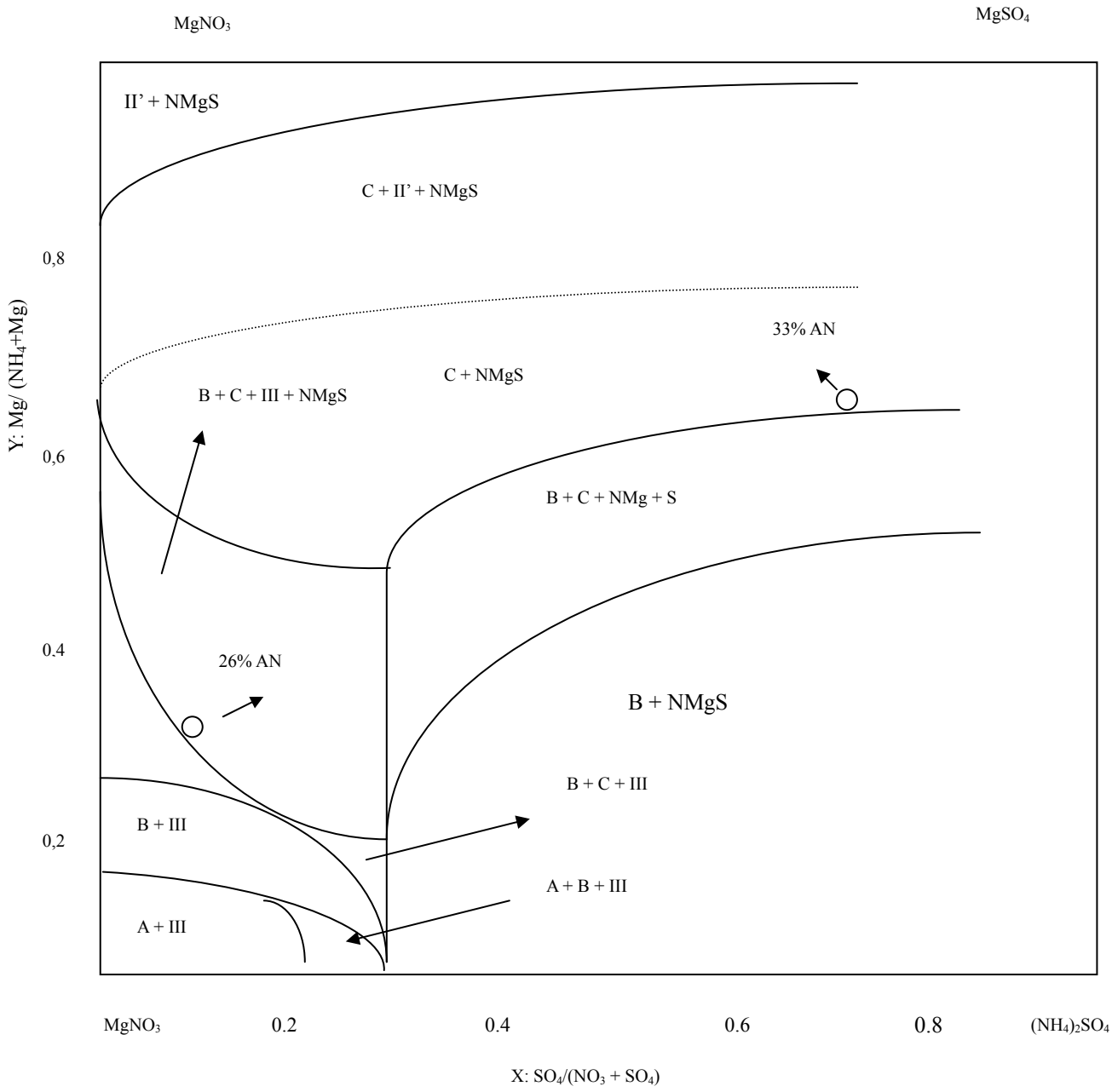


Figure 2. Compounds Immediately After Cooling To Room Temperature From 150 ℃

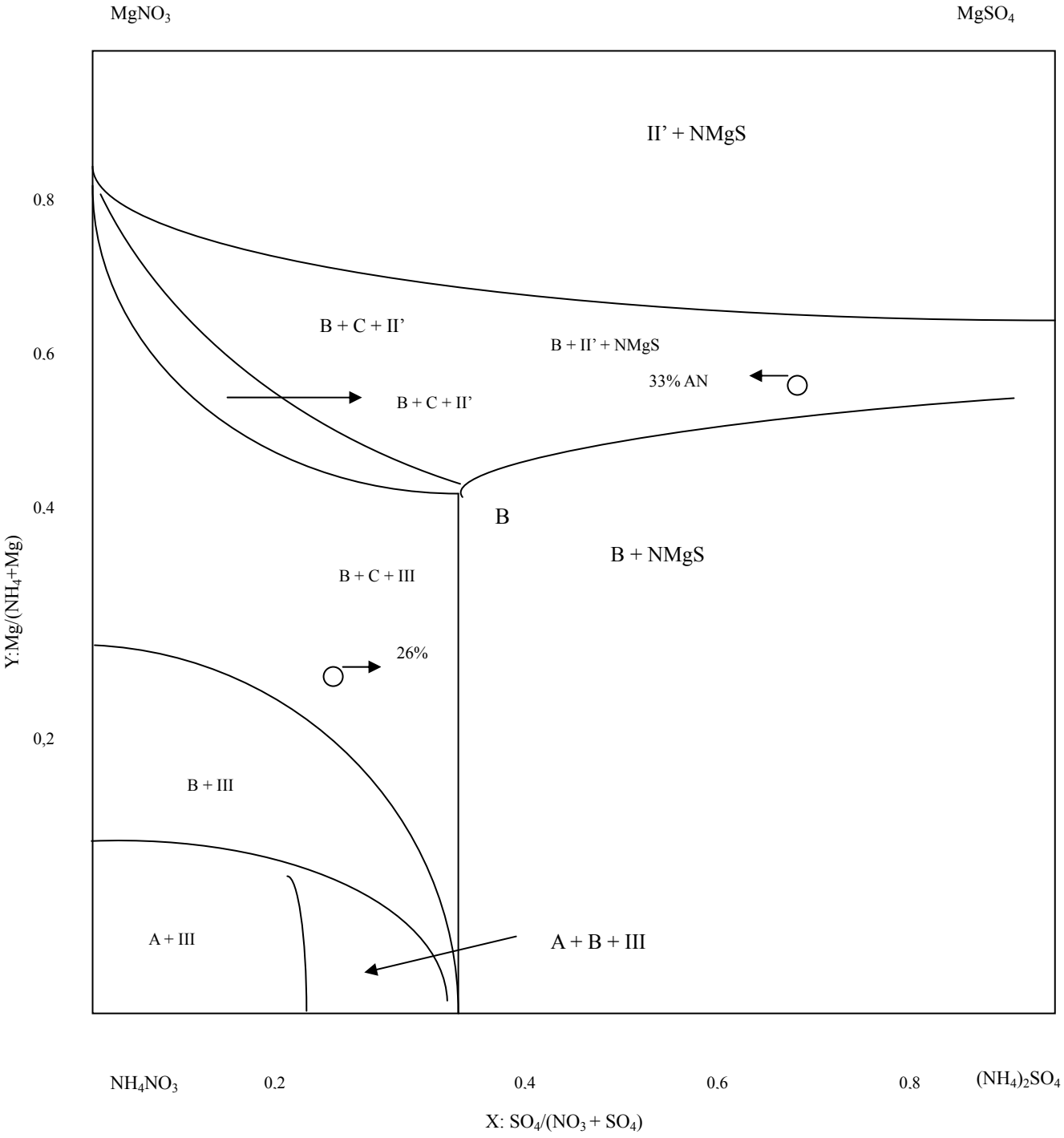


Figure 3. Compounds Stable at Room Temperature

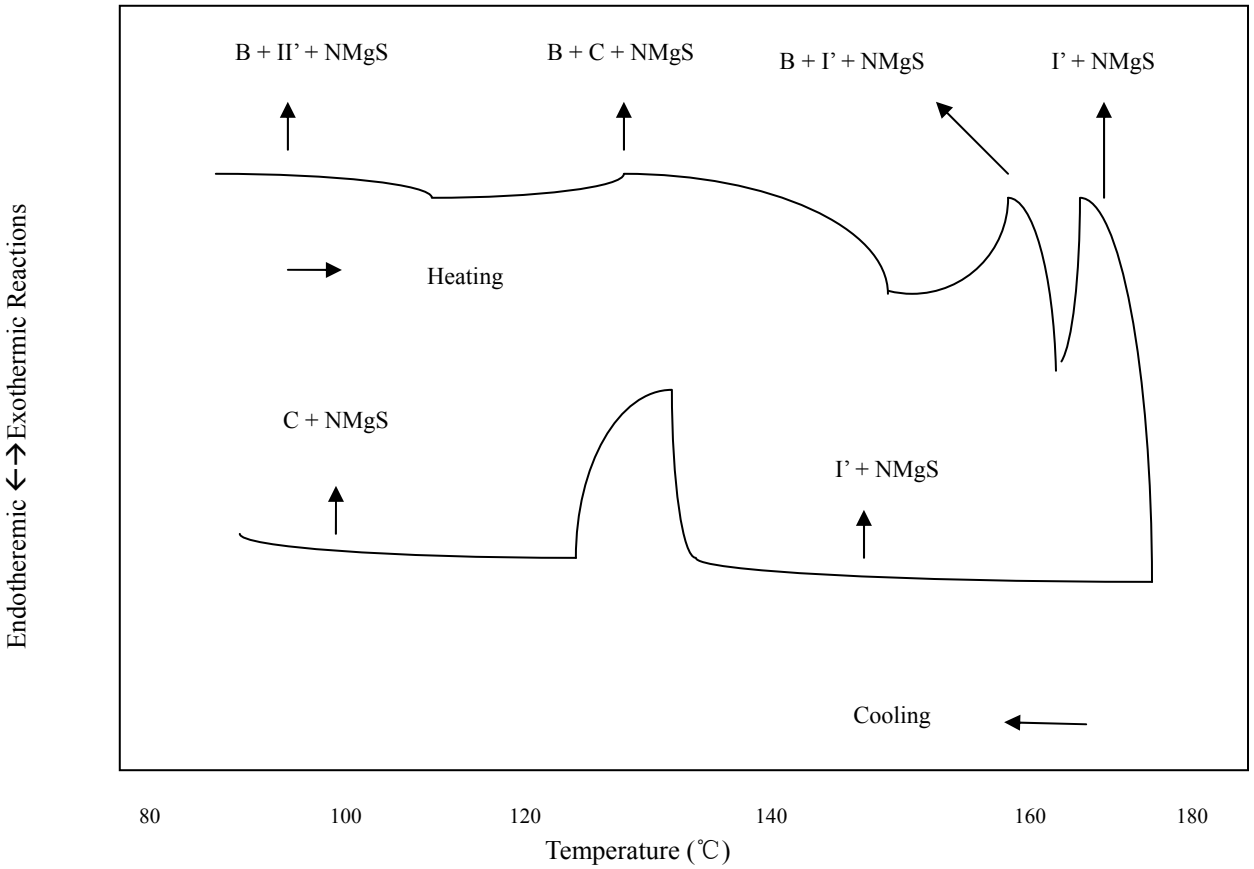


Figure 4. Differential Thermal Analysis Curve of A Sample X: 0.33, Y = 0.5

(I' means I – MgN)

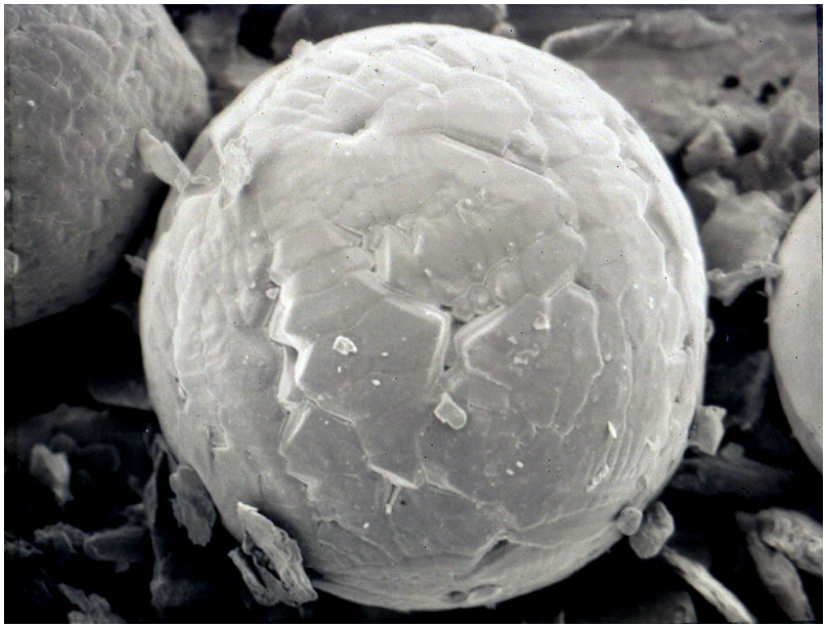
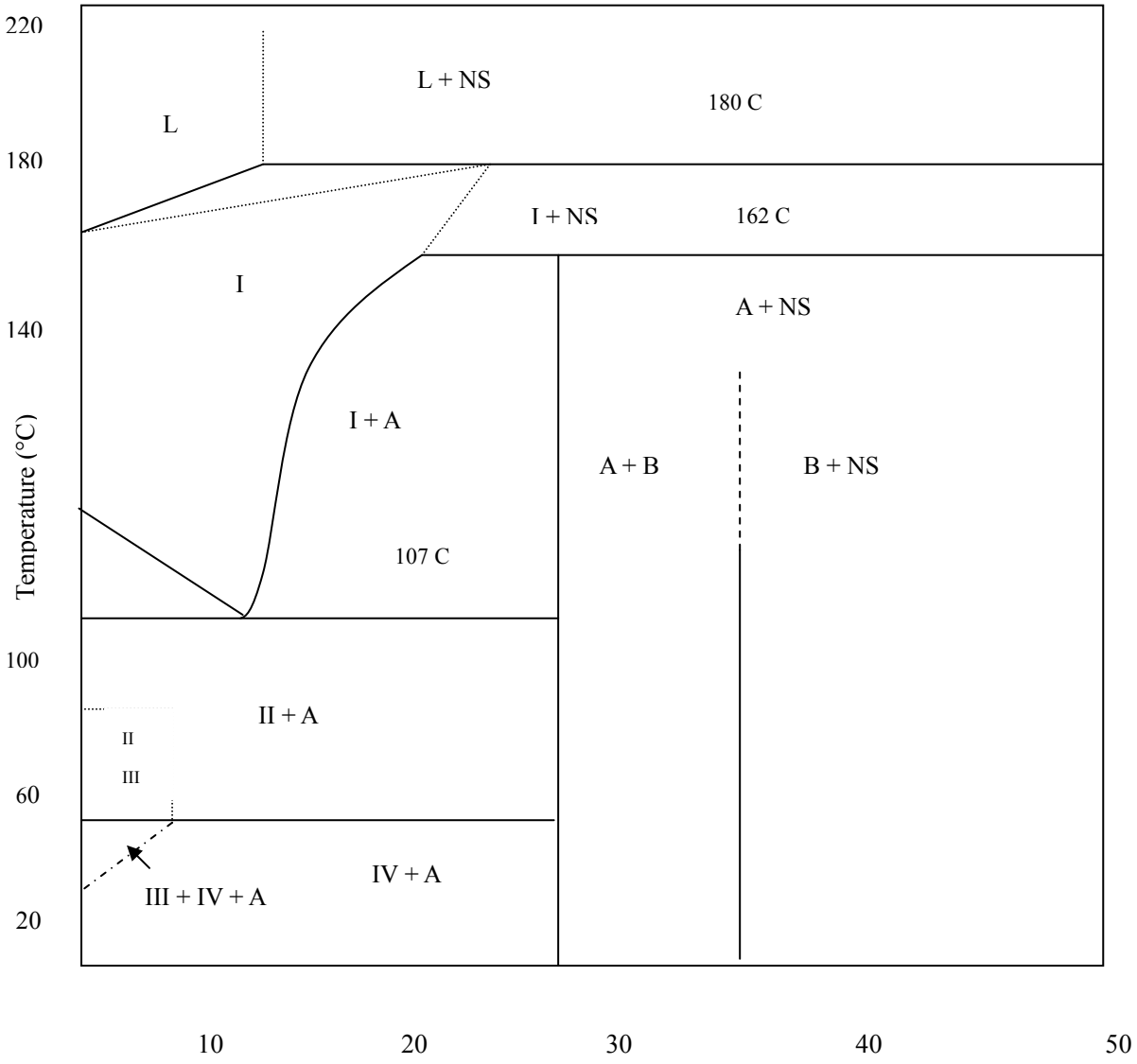


Figure 5. White Blister on the Surface Of Prilled AN



$NH_4NO_3 \cdot (NH_4)_2SO_4$ mole %

Figure 6. Phase Diagram of $NH_4NO_3 \cdot (NH_4)_2SO_4$ System

I: Form I NH_4NO_3 A: 3 $NH_4NO_3 \cdot (NH_4)_2SO_4$

II: Form I NH_4NO_3 B: 2 $NH_4NO_3 \cdot (NH_4)_2SO_4$

III: Form III NH_4NO_3 L: Liquid

IV: Form III NH_4NO_3 NS: $(NH_4)_2SO_4$

 ISSN 1916-9698 E-ISSN 1916-9701

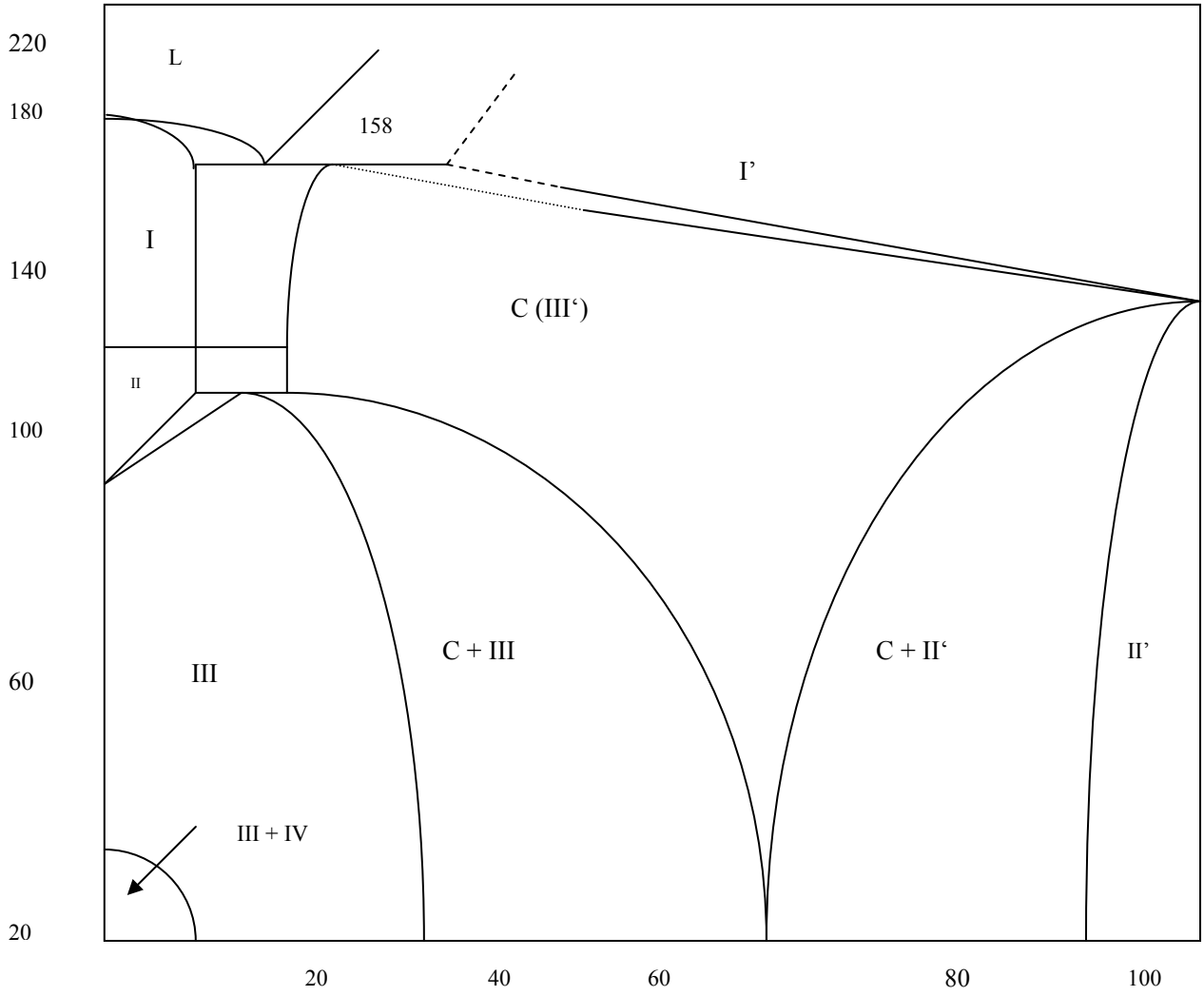


Figure 7. Phase Diagram of $NH_4NO_3 \cdot Mg(NO_3)_2$ System

I': Form I $Mg(NO_3)_2$

II': Form II $Mg(NO_3)_2$

III': Form III $Mg(NO_3)_2$

C: $NH_4NO_3 \cdot 2Mg(NO_3)_2$