Thermodynamic Justification for the Production of Sulfur-containing Nitrogen-Phosphorus Fertilizers

Arislanov Akmaljon Saidbaevich
Senior Lecturer, Namangan Institute of Engineering and Technology, Uzbekistan

Shamshidinov Israiljan Turgunovich
Doctor of Technical Science professor, Namangan Engineering and Construction Institute, Uzbekistan

Isomiddinov Oybek Najmiddin og'li
Student of 9bu-20 group, Namangan Institute of Engineering and Technological, Uzbekistan

Abstract:

Objective. The article introduces a predetermination of the possibility of a reaction and therefore of the salt composition of the final products which, due to the complexity of the original and final products, is extremely difficult. Therefore, the reaction of tricalcyphosphate, calcium carbonate, magnesium, iron oxides and aluminium, i.e. those which are possible during the production of phosphorus sulfur-containing fertilizers, was analysed.

Methods. Thermodynamic analysis makes it possible to predetermine the possibility of a reaction and therefore the salt composition of the final products, which are extremely complex due to the complexity of the original and final products.Therefore, the reaction of tricalcyphosphate, calcium carbonate, magnesium, iron oxides and aluminium, i.e. those which are possible during the production of phosphorus sulfur-containing fertilizers, was analysed.

For each reaction we found the isobarn-isothermic potential and judged the possibility of a reaction (negative value G).Thermodynamic calculations of possibilities of formation of phosphates and sulphates of calcium, magnesium, iron, aluminium in process of production of sulfur-containing nitrogen-phosphorus fertilizers were carried out according to simplified formula $\Delta G=\Delta H-T\Delta S$ Thermal capacity excluded.

Results. The phosphates of the Central Kyzylkum differ substantially from the phosphate Karatau in chemical composition and therefore the main contribution to the thermal effect of the interaction of phosphate with phosphate and sulfuric acids are the processes of interaction with tricalcyphosphate and calcium carbonate.

Conclusion. 96% the thermal effect of the interaction of phosphate CK is the interaction of tricalcyphosphate and calcium carbonate with phosphoric acid and 95,4% with sulphuric acid. The heat effects of the other components do not exceed 4-4,6%.

Keywords: thermodynamics, thermodynamic calculations, thermodynamic characteristics, thermodynamic analysis, phosphate Karatau and Kyzylkum, isobarn-isothermicpotential, Tricalcyphosphate, sulphuric acid, phosphoric acid, nitric acid, calcium and magnesium-containing minerals, heat-treated dolomite, calcium and magnesium hydro phosphate, thermal effect.

Introduction. The processes for producing sulfur-containing nitrogen-phosphorus-containing fertilizers by decomposing phosphate raw material with phosphate and sulphuric acids are based on the reaction of the components of the raw material with acids, which may lead to the formation of various compounds of phosphates and sulphates,of the raw material. Literary sources do not adequately cover the theory of the processes to be studied and very little information is available in this area.

Methods. Thermodynamic calculations carried out when extracting phosphoric acid from washed Central Kyzylkumphosphate. It is shown that the greatest thermal effect is observed in the interaction of calcium oxide, magnesium and calcium silicate with sulphuric acid, that the thermal effect of free calcium oxide is equal to the contribution of burned phos-Concentrate that the free oxide of calcium is more actively involved with water than with nitric and phosphoric acids [1].

Thermodynamic calculations of the processes of decomposition of calcium and magnesium-containing minerals with phosphoric acid at a temperature of 298 K were carried out and the thermodynamic characteristics of interaction of components of minerals with acid were determined.

Thermodynamic analysis has shown that the most likely reactions in the interaction of calcium and magnesium carbonates are processes that produce dihydrophosphates of calcium and magnesium, with magnesium carbonate more easily interacting with phosphoric acid.

Reactions of the interaction of calcium and magnesium carbonates with orthophosphoric acid occuranologically in the formation of calcium and magnesium hydrophosphates. G formation of magnesium hydrophosphate is less than formation of calcium hydrophosphate. In the interaction of calcium carbonates and magnesium, the probability of formation of dihydrophosphates is higher than that of hydrophosphates. To produce calcium and magnesium hydrophosphates, the phosphoric acid requirement shall be less than 2 times the dihydrophosphate requirement at the same temperature – 298 K.

Based on chemical analysis, the calcareous compositions of chalk, limestone and dolomite and their compositions after heat treatment are calculated, the heat emitted in the formation of dihydrophosphates and hydrophosphates of calcium and magnesium, and their contribution to the overall heat effect of the process.

The thermal effects of the interaction of calcium carbonate and magnesium in the composition of dolomite are 56.34-63.71% of the total thermal effect. The thermal effect of heat-treated dolomite is 511.0 kJ/kg for calcium and magnesium dihydrophosphates and 481.0 kJ/kg for hydrophosphates.

Their contribution to the overall heat effect of the process is greater than that of the non-flammable dolomite and is 70,06-71,82% [2].

The main minerals composing the phosphate ores of the Central Kyzylkum are:calcite (30-50%), Fluorcarbonatapatitis (25-55%) and clay minerals (3-25%); secondary minerals - gypsum, gotit, pyrite, quartz. The main useful mineral, fluorcarbonatapatite (Francolite), is concentrated in granulated material. Cement is represented by a fine or pelite material consisting of calcite and clay [3].

Results.Thermodynamic analysis makes it possible to predetermine the possibility of a reaction and therefore the salt composition of the final products, which are extremely complex due to the complexity of the original and final products. Therefore, the reaction of tricalcyphosphate, calcium carbonate, magnesium, iron oxides and aluminium, i.e. those which are possible during the production of phosphorus sulfur-containing fertilizers, was analysed.

For each reaction we found the isobarn-isothermic potential and judged the possibility of a reaction (negative value G).Thermodynamic calculations of possibilities of formation of phosphates and sulphates of calcium, magnesium, iron, aluminium in process of production of sulfur-containing nitrogen-phosphorus fertilizers were carried out according to simplified formula $\Delta G=\Delta H\text{-}T\Delta S$ Thermal capacity excluded. The results are presented in the table 3.1.

Thermodynamic analysis has shown that the most likely reactions to the interaction of tricalcyphosphate, calcium and magnesium carbonates, iron oxides and aluminium are processes that form calcium and magnesium dihydrophosphates, iron phosphates and aluminium, andtricalcyphosphate is easier to interact with phosphorus and sulfuric acids. Isobarn-insulated reaction potential of tricalcyphosphate is smaller (-197 and -220 kJ/mol) than that of calcium carbonate, magnesium, iron oxides, aluminium with phosphoric acid (-88 and-160 kJ/mol).

Table 1. Thermodynamic characteristics of the main reactions in phosphorus sulphide decomposition of phosphate raw materials

№ p/p	reaction	$\Delta H°_{298}$, kJ/mol	$\Delta S°_{298}$,J/molhail	$\Delta G°_{298}$, kJ/mol
When the phosphate feedstock is degraded with phosphoric acid				
1.	$Ca_3(PO_4)_2+4H_3PO_4+3H_2O=3Ca(H_2PO_4)_2\cdot H_2O$	-142	-109	-197
2.	$CaCO_3+2H_3PO_4=Ca(H_2PO_4)_2\cdot H_2O+CO_2$	-38	176	-88
3.	$MgCO_3+2H_3PO_4+H_2O=Mg(H_2PO_4)_2\cdot 2H_2O+CO_2$	-48	76	-94
4.	$Fe_2O_3+2H_3PO_4=2FePO_4+3H_2O$	-70	105	-101
5.	$Al_2O_3+2H_3PO_4=2AlPO_4+3H_2O$	-93	121	-127
When the phosphate feedstock is decomposed with sulphuric acid				
1.	$Ca_3(PO_4)_2+2H_2SO_4+5H_2O=3Ca(H_2PO_4)_2\cdot H_2O+2CaSO_4\cdot 2H_2O$	-268	-252	-220
2.	$CaCO_3+H_2SO_4+H_2O=CaSO_4\cdot 2H_2O+CO_2$	-110	89	-134
3.	$MgCO_3+2H_2SO_4+H_2O=MgSO_4\cdot 7H_2O+CO_2$	-137	80	-119
4.	$Fe_2O_3 + 2H_2SO_4 + H_2O = 2Fe_2(SO_4)_3$	-183	65	-154
5.	$Al_2O_3 + 2H_2SO_4 + H_2O = 2Al_2(SO_4)_3$	-187	-72	-160

Iron oxides and aluminium are more likely to interact with phosphoric acid than calcium and magnesium carbonates. The isobarn-insulated potential of iron and aluminium oxides is -101 J/mol and -127 J/mol, while the values for magnesium carbonates and calcium are -94 J/mol and -88 J/mol.

The probability of interaction of iron oxides and aluminium with sulphuric acid is also slightly higher than in the interaction of calcium and magnesium carbonates.

The results show that when the components of phosphate raw material (phosphate Karatau and central Kyzylkum) interact with phosphoric acid, all the components are subjected to interaction to form acid-like forms,while the interaction with sulphuric acid produces calcium sulphate dihydrate in the precipitation.

Table 2 shows the thermal effects of the reactions of the main components of Caratau phosphate with phosphate and sulphuric acids, showing that the main contribution to the thermal effect of Caratau phosphate interaction with phosphate phosphate and sulfuric acids contribute to the interaction of acids with tricalcyphosphate 89.8% and 85.9% respectively with phosphoric and sulphuric acids. The contribution of the rest of the raw materials to the heat effect is small and is 10,2% и 14,1%.

Table 2. Thermal effects of Karatau phosphate reaction with phosphoric and sulphuric acid

Main components of phosphate	Average chemical composition, by mass. %	Heat at decomposition, kJ/kg	Contribution to total heat, %
When the phosphate feedstock is degraded with phosphoric acid			
$Ca_3(PO_4)_2$	55,5	142·0,555=78,8	89,8
$CaCO_3$	11,8	38·0,118=4,5	5,1
$MgCO_3$	5,5	48·0,055=2,6	3,0
Fe_2O_3	0,8	70·0,008=0,6	0,7
Al_2O_3	1,3	93·0,013=1,2	1,4
other	25,1	-	-
Total:		**87,7**	**100**
When the phosphate feedstock is decomposed with sulphuric acid			
$Ca_3(PO_4)_2$	55,5	268·0,555=148,7	85,9
$CaCO_3$	11,8	110·0,118=13,0	7,5
$MgCO_3$	5,5	137·0,055=7,5	4,3
Fe_2O_3	0,8	183·0,008=1,5	0,9
Al_2O_3	1,3	187·0,013=2,4	1,4
other	25,1	-	-
Total:		**173,1**	**100**

Table 3 shows the thermal effects of reactions of phosphate reaction of Central Kyzylkum with phosphoric and sulphuric acids.

Table 3. Thermal Effects of Central Kyzylkum Phosphate Reaction with Phosphoric and Sulphuric Acid

Main components of phosphate	Average chemical composition, by mass. %	Heat at decomposition, kJ/kg	Contribution to total heat, %
When the phosphate feedstock is degraded with phosphoric acid			
$Ca_3(PO_4)_2$	38	142·0,38=54,0	73,1
$CaCO_3$	44,5	38·0,445=16,9	22,9
$MgCO_3$	1,9	48·0,019=0,9	1,2
Fe_2O_3	1,0	70·0,01=0,7	0,9
Al_2O_3	1,5	93·0,015=1,4	1,9
other	13,1	-	-
Total:		**73,9**	**100**
When the phosphate feedstock is decomposed with sulphuric acid			
$Ca_3(PO_4)_2$	38	268·0,38=101,8	64,4
$CaCO_3$	44,5	110·0,445=49,0	31,0
$MgCO_3$	1,9	137·0,019=2,6	1,7
Fe_2O_3	1,0	183·0,01=1,8	1,1
Al_2O_3	1,5	187·0,015=2,8	1,8
other	13,1	-	-
Total:		**158,0**	**100**

Discussion. The phosphates of the Central Kyzylkum differ substantially from the phosphate Karatau in chemical composition and therefore the main contribution to the thermal effect of the interaction of phosphate with phosphate and sulfuric acids are the processes of interaction with tricalcyphosphate and calcium carbonate.

Conclusion. The results show that when the components of phosphate raw material (phosphate Karatau and central Kyzylkum) interact with phosphoric acid, all the components are subjected to interaction to form acid-like forms,while the interaction with sulphuric acid produces calcium sulphate dihydrate in the precipitation.96% the thermal effect of the interaction of phosphate CK is the interaction of tricalcyphosphate and calcium carbonate with phosphoric acid and 95,4% with sulphuric acid. The heat effects of the other components do not exceed 4-4,6%.

List of Used Literature

1. Thermodynamic Justification of the Process of Extraction of Phosphoric Acid from Central Kyzylkum Phosphate // Universum: Technical Sciences : Electron. Scientifically.Jurn.Volynskova N.V. [etal.].2019. № 1(58). URL: *http://7universum.com/ru/tech/archive/item/6856*
2. Mamurov B. A. Development of calcium and magnesiphosphate fertilizer technology using local carbonate raw materials. Diss. kand.techn.science. - Namangan, 2020. – 146c.
3. Geology and minerals of the Republic of Uzbekistan / T.N. Dolimov, T.S. Shayakubov et al.: Redkol.: T.S. Shayakubov (Gl.) and others. - T.: University, 1998. – 724c.
4. Gafurov K., Shamshidinov. I.T., Arislanov A.S. Research and development of obtaining complex defluorinated fertilizers from phosphorites of Karatau. Research report on the state budget, state register No. 01.88.0017867. Namangan, 1991 one. Antipenko G.L., Markov S.S. Possible ways of rational use of fluorine sources. -Khim.prom.-1974. -№9. - P.43 (638).
5. Gafurov K., Shamshidinov IT, Arislanov A.S. Sulfuric acid processing of high-magnesium phosphates and obtaining NPS-fertilizers based on them. Monograph. Publishing house "Istedodziyo press"Namangan-2020... P.26-27
6. Shamshidinov I.T., Kan N.R., Usmanov I.I., Mirzakulov Kh.Ch. Investigation of the process of defluorination of extraction phosphoric acid from phosphorites of the Central Kyzyl Kum // Uzbek chemical journal. - Tashkent, 2017. - No. 2. - P. 47-54.
7. Erkaev A.U., Mirzakulov Kh.Ch. Dephorization of extraction phosphoric acid from Karatauphosphorites. / Ed. Uzbek. chem. zhurn. - Tashkent, 1992.-- 15 p. Dep. in VINITI, 5.02.1992. - No. 403 B-92.
8. Mirzakulov Kh.Ch. Development of an effective technology for defluorination of extraction phosphoric acid from Karatauphosphorites. / Author's abstract. diss…. Cand.tech. sciences. - Tashkent, 1993 .-- 25 p.
9. Erkaev AU, Mirzakulov Kh.Ch., Rakhimov U. Intensification of the pulp thickening process during defluorization of extraction phosphoric acid from Karatauphosphorites. / All-Union. conf. on the chemical technology of inorganic substances: Abstracts. report - Kazan, May 29-31, 1991 - P. 57.
10. Mirzakulov Kh.Ch., Erkaev A.U., Mirkhuzhaev M.M. Phosphorus extraction by acids sinning fluorosislanningyangi roasting technologies. // Ўzbekiston FA 50 yilligigabaғishlangan I yosholimlarvamutahassislarninganjumani. Chit-93 Maruzalarmatni. May 27-28, 1993 Toshkent. - B. 15.
11. Gafurov K., Shamshidinov. I.T., Arislanov A.S. Defluorination of extraction phosphoric

acid during its extraction. "VestnikFerPI", Fergana, 2005, No. 1

12. Gafurov K., Arislanov A., Shamshidinov I. Reduction of fluoride compounds in phosphogypsum // Scientific and technical journal FerPI. - Fergana, 2004. - No. 3. - S. 63-66.
13. Gafurov K. Resource saving and improvement of ecological purity of products of processing of phosphorites of Karatau. Author's abstract. dis. ... doct. tech. sciences. - Tashkent, 1990 .-- 52 p.
14. 14 Arislanov A.S., Rezhabbaev M., Soliev M., Abdurazzakova M. Defluorination of EPA during its extraction. Scientific electronic journal "Academic journalism". - Ufa: Aeterna, Russia-2018.-P.25
15. Arislanov A.S., Zhuraboev F., Dzhuraev M. Defluorination of EPA of Kyzylkumphosphorites in the process of decomposition: Collection of articles on the results of the International scientific and practical conference (Chelyabinsk, May 26, 2018) in Part 1 - Sterlitamak: AMI, 2018 .--267 p.
16. Gafurov K. Defluorinated fertilizers from phosphorites of Karatau. - Tashkent: FAN, 1992 .-- 200 p.
17. Patent No. 5698 UZ. Method of obtaining extraction phosphoric acid / Gafurov K., Shamshidinov I.T., Arislanov A., Mamadaliev A. (UZ) / 1998. - Byul. No. 4.
18. Gafurov K. Resource saving and improvement of ecological purity of products of processing of phosphorites of Karatau. Dis. ... doct.tech. sciences. - Tashkent, 1990 .-- 52 p.