Exergy analysis of the process of production of dicalcium phosphate dihydrate by decomposition of rock phosphate with hydrochloric acid

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ABSTRACT

Dicalcium phosphate dihydrate (precipitate) is used in agriculture as an additive to livestock food and as phosphorous containing mineral fertilizer. There are several methods for its production depending on the mineral acid used for the decomposition of natural phosphate. The present paper discusses a process where natural phosphate is decomposed using hydrochloric acid. This is a chemical technological process consuming large amount of energy. To assess its exergy efficiency, the exergy method is used. The aim of the work is to make exergy analysis of the process of production of precipitate by decomposition of rock phosphate with hydrochloric acid. The material, energy and exergy balances are made for the individual stages of precipitate preparation and for the whole process. The internal and external exergy losses are calculated. The exergy efficiency is low - 2.33 %. Suggestions are made which could increase the exergy efficiency up to 21 %.　　© 2014 Trade Science Inc. - INDIA

KEYWORDS

INTRODUCTION

The normal growth of livestock and birds requires adequate nourishment. For this purpose, mineral salts are added to their food to accelerate their growth, increase their productivity and improve production quality. These salts are from the group of phosphorous containing mineral substances the lack of which in animal organisms sharply decreases their productivity, as well as their resistance to many diseases. The most widely applied forage phosphate is the calcium hydrogen phosphate with two molecules of crystallization water ($CaHPO_4.2H_2O$) called dicalcium phosphate dihydrate or precipitate in industry and agriculture. It contains the two nutritious elements phosphorus and calcium in the

most favorable ratio to satisfy the needs of stock breeding. Dicalcium phosphate dihydrate can also be used as phosphorous mineral fertilizer containing 41.25 % digestible P_2O_5. The dicalcium phosphate dihydrate (precipitate) for nutritious purposes contains 43-47 % P_2O_5 which is soluble in 0.4 % hydrochloric acid – a concentration corresponding to that in animal gastric juice[1,2].

There are various methods for preparation of dicalcium phosphate dihydrate depending on the mineral acid used to decompose natural phosphates. The method used affects the composition, purity and digestibility of the product obtained (dicalcium phosphate dihydrate). The most famous production method is known as "wet acid" decomposition where the rock phosphate (apatite or phosphorite) interacts with sulfuric acid. The

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phosphoric acid obtained is then concentrated and purified from contaminants. Further, it interacts with a source of calcium like calcium oxide (CaO) or limestone ($CaCO_3$). The purity of the phosphoric acid used strongly influences the quality of the product obtained. Besides, the production of pure phosphoric acid is quite expensive. For this reason, another method for preparation of dicalcium phosphate dihydrate (precipitate) has been recently developed using the cheaper hydrochloric acid for the decomposition of rock phosphates[3,4]. The dicalcium phosphate dihydrate ($CaHPO_4.2H_2O$) obtained is of high purity.

It is well known that the chemical technological processes have usually high exergy consumption. To estimate their exergy efficiency, one of the modern methods of thermodynamic analysis is used – the exergy method. Its use provides possibilities to determine the exergy losses and the exergy efficiency for every stage of a chemical technological production, and then recommend measures for decrease or elimination of the high exergy losses to increase the exergy efficiency. The method is more and more widely used for the determination of the exergy consumption of technical and technological processes[5-16].

The aim of the present work is to assess the exergy efficiency of the process of production of dicalcium phosphate dihydrate by decomposition of rock phosphate with hydrochloric acid.

The literary survey showed than this process has not been estimated from the point of view of exergy consumption. In an earlier publication[17], the author has reported for the exergy analysis of the production of dicalcium phosphate dihydrate (precipitate) but one obtained from phosphoric acid and calcimine.

DESCRIPTION OF THE TECHNOLOGICAL PROCESS

A flow diagram of the process of production of dicalcium phosphate dihydrate is presented in Figure 1.

The initial materials used for the production of dicalcium phosphate dihydrate ($CaHPO_4.2H_2O$) are hydrochloric acid and natural phosphate material (phosphorite). Phosphorite, hydrochloric acid and water are mixed at precise ratio and the mixture is fed into Reactor I. The product obtained is phosphoric acid. The reaction of phosphorite decomposition is exothermic (it releases heat) and proceeds according to the fol-
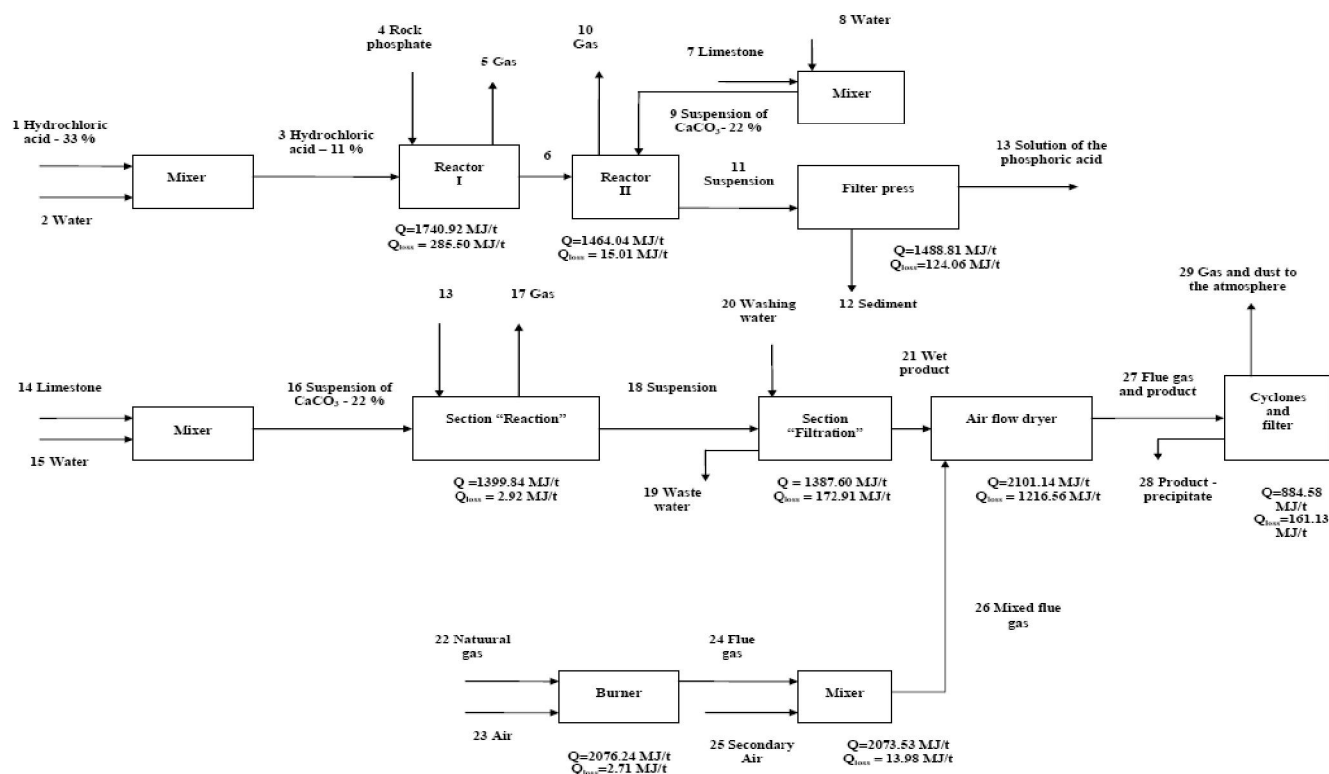

Figure 1 : Schematic diagram of dicalcium phosphate dihydrate production

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lowing chemical equation:

$$Ca_5F(PO_4)_3 + 10HCl = 3H_3PO_4 + 5CaCl_2 + HF \qquad (1)$$

The suspension obtained is then transferred to Reactor II. Reaction (1) occurs at temperatures 40-50 ^{0}C. Under these conditions, HF remains in the solution and reacts with the metasilicic acid (H_2SiO_3) which is generated by the acidic decomposition of some silicates contained in the phosphate material (phosphorite). Thus, tetrafluorsilane (SiF_4) and fluorosilicic acid are formed according to the reaction:
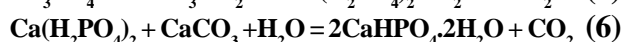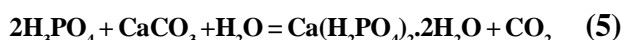
$$2H_2SiO_3 + 10HF = SiF_4 + H_2SiF_6 + 6H_2O \qquad (2)$$

The ions of Na^+, K^+ and Ca^{2+} contained in the rock phosphate react with the fluorosilicic acid to give slightly soluble silicon fluorides. To remove fluorine from the system, the suspension obtained is neutralized with a suspension of $CaCO_3$ until pH 0.8-1.2 in Reactor II.

$$2HF + CaCO_3 = CaF_2 + H_2O + CO_2 \qquad (3)$$
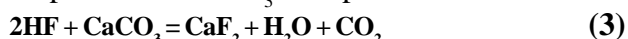
Intense foam formation can be observed in the reactor due to the release of CO_2. With this process, the following side reaction takes place:

$$(Al, Fe)_2O_3 + 2H_3PO_4 + H_2O = 2(Al, Fe)PO_4.2H_2O \qquad (4)$$
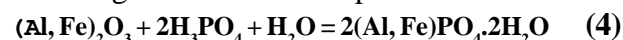
The mixture of solid and liquid phases is the separated in a filter press. The solid residue is wasted while the liquid phase containing phosphoric acid is used as initial material for the next stage of the process– neutralization with a suspension of calcium carbonate. The process is performed in the "Reaction" section to obtain dicalcium phosphate dihydrate ($CaHPO_4.2H_2O$) as precipitate. pH is maintained in he range 3.2-3.5. The process occurs according to the following chemical reactions:

$$2H_3PO_4 + CaCO_3 + H_2O = Ca(H_2PO_4)_2.2H_2O + CO_2 \qquad (5)$$
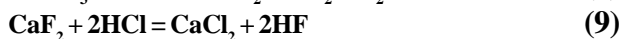$$Ca(H_2PO_4)_2 + CaCO_3 + H_2O = 2CaHPO_4.2H_2O + CO_2 \qquad (6)$$

The suspension obtained is then separated in the "Filtration" section using centrifuges. The waste water from the centrifuges is dumped into the acidic drainage. The solid phase residue is wet precipitate containing 10-15 % moisture. Using conveyor belt, the wet precipitate is transferred to the inlet of a drying apparatus type "Air flow tube" where flue gases are used to dry it down to 3.0 % moisture content. The fuel used is natural gas. The precipitate is removed from the flue gas by a series of cyclones and sleeve filter. Thus, the emissions of precipitate powder in the atmosphere are reduced to a minimum. The end product is collected in a hopper and then transported for packaging.

MASS AND HEAT BALANCES

The materials and heat balances are calculated for all the stages of precipitate production. The results obtained for the materials balance are presented in TABLE 1 while the heat loads and heat losses in the main devices – in Figure 1.

The materials balance of the process of dicalcium phosphate dihydrate production are elaborated using real data. All the results are calculated per ton of the product - dicalcium phosphate dihydrate.
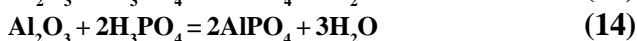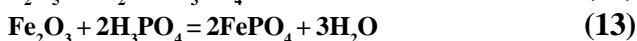
The hydrochloric acid decomposition of phosphorite takes place in Reactor I by reaction (1). The theoretical consumption of hydrochloric acid with concentration of 11 wet % (point 3 in Figure 1) is determined by the content of CaO and contaminants in the phosphorite according to the following reactions:

$$CaO + 2HCl = CaCl_2 + H_2O \qquad (7)$$
$$CaCO_3 + 2HCl = CaCl_2 + CO_2 + H_2O \qquad (8)$$
$$CaF_2 + 2HCl = CaCl_2 + 2HF \qquad (9)$$
$$MgO + 2HCl = MgCl_2 + H_2O \qquad (10)$$

Taking the CO_2 content in the initial phosphate material, the content of CaO in $CaCO_3$ is calculated using reaction (11) while the remainder of CaO is free to react with the hydrochloric acid by reaction (7).

$$CaO + CO_2 = CaCO_3 \qquad (11)$$

All the chemical reactions taking place in the reactor are irreversible so the calculations are stoichiometric according to the reactions. The total amount of phosphorus introduced into the system with the phosphorite is not transformed into phosphoric acid. Phosphorus is introduced as phosphorus pentoxide (P_2O_5). Part of it reacts with the iron and aluminium oxides (R_2O_3) contained as alloys in the initial material to give iron and aluminium phosphates which remain in the suspension obtained (point 6 in Figure 1). The reactions are as follows:

$$P_2O_5 + 3H_2O = H_3PO_4 \qquad (12)$$
$$Fe_2O_3 + 2H_3PO_4 = 2FePO_4 + 3H_2O \qquad (13)$$
$$Al_2O_3 + 2H_3PO_4 = 2AlPO_4 + 3H_2O \qquad (14)$$

The rock phosphate introduced is not fully decomposed. It is calculated that the coefficient of decomposition of the phosphate material is about 90 %. The rest is not decomposed and passes to the insoluble remainder. The water introduced in Reactor I with the inflows is consumed for the formation of phosphoric acid ac-

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TABLE 1 : The in- and outgoing flows of the precipitate production

Flow, [1]	Temperature, °C	HCl	CaCO3	H2O	P2O5	CaO	MgO	R2O3	CaF2	SiO2	Insoluble residue	CO2	SO3	Na2O	K2O	Amount, kg.t⁻¹ product	Exergy flow, kJ.kg⁻¹
1. Hydro-chloric acid	25	33.00		67.00												2998.98	942.00
2,8,15 Water	18			100.00												5997.74 38.90 1995.26	161.65
3. Hydro-chloric acid	30	11.00		89.00												8996.72	431.48
4. Rock phosphate	30			1.00	28.00	47.00	0.70	0.55	7.00	2.00	3.00	7.00	2.50	1.10	0.15	1645.94	1944.52
7,14. Limestone	25		98.88	0.30			0.45	0.04		0.33						11.14 570.96	134.46
9,16. Suspension of CaCO3	30		22.00	77.82			0.10	0.01		0.07						50.04 2566.22	161.67

Flow	Temp, °C	$CaF_2.H_2O$	H2O	RPO_4	CaO	$CaSO_4$	$MgCl_2$	CaF2	SiO2	Insoluble	HF	$CaCl_2$	Na_2SiF_6	K_2SiF_6	Amount	Exergy
6. Suspension	50		76.15	3.88	0.17	0.67	0.23	0.04		4.12	0.06	14.15	0.47	0.06	10430.72	393.55
11. Suspension	50	0.10	76.20	3.86	0.17	0.67	0.23	0.04		4.10	0.02	14.09	0.47	0.05	10475.95	380.73
12. Sediment	40	0.60	23.08	1.02		3.99	1.39	0.25		24.48		42.07	2.82	0.30	1754.58	444.50
13. Solution of the phosphoric acid	48		86.88	4.64							0.02	8.46			8721.37	339.19

Flow	Temp, °C	H2O	P2O5	CaO	MgO	F	Insoluble residue	$CaHPO_4.2H_2O$	Amount	Exergy
18. Suspension	43	84.43	0.04	0.02	0.01	0.02	8.80	6.68	11039.12	222.41
19. Waste water	40	92.47	0.04	0.03		0.02		7.44	883873.16	217.13
20. Washing water	18	100.00							873952.00	161.65
21. Wet product	40	13.03				0.09		86.88	1117.76	231.02
28. Product – precipitate	55	2.90				0.10		97.00	1000.00	230.96

Flow	Temp, °C	SiF_4	HF	H2O	O_2	N_2	CH_4	C_2H_6	C_3H_8	C_4H_{10}	C_5H_{12}	C_6H_{14}	CO_2	Amount	Exergy
5. Gas	50	6.52	1.26	37.86									54.36	211.94	602.26
10. Gas	50												100.00	4.85	453.42
17. Gas	43												100.00	248.47	453.66
22. Natural gas	25					1.30	94.41	2.22	1.15	0.53	0.13	0.05	0.21	42.41	51199.93
23. Air	25			1.47	22.98	75.55								834.42	0.00
24. Flue gas	1235			12.02	2.85	71.97							13.16	876.83	1038.46
25. Secondary Air	25			1.47	22.98	75.55								7645.73	0.00
26. Mixed Flue gas	213			2.56	20.89	75.20							1.35	8522.56	48.66
27. Flue gas and product	85			3.77	18.47	66.48		0.01	10.07				1.20	9640.33	35.55
29. Gas and dust to the atmosphere	75			3.87	20.61	74.17			0.01				1.34	8640.33	8.96

cording to reaction (12) (153.97 kg/t product), a small part of it evaporates and passes into the gaseous phases (flow 5 – 80.24 kg/t product) and the remaining part is liquid phase in the suspension (flow 6- 7789.23 kg/t product). In Reactor II, the inflowing suspension is purified from the HF it contains. The degree of purification is 80 % and the main reaction is:
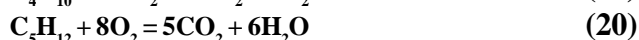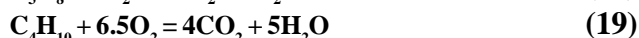
$$2HF + CaCO_3 = CaF_2.H_2O + CO_2 \qquad (15)$$

The amounts of $CaF_2.H_2O$ and CO_2, as well as the amount of $CaCO_3$ consumed are calculated stoichiometrically from reaction (15). The whole amount of $CaCO_3$ introduced interacts by reaction (15).

The filter press separates the liquid and the solid phases. The solid phase is called precipitate or slime. It carries 50 % of the $CaCl_2$ introduced and 30 % of the water.

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In the "Reaction" section, the main reactions (5) and (6) between the phosphoric acid and calcium carbonate take place to obtain dicalcium phosphate dihydrate (precipitate). The required amount of calcium carbonate solution which should be introduced and the amount of precipitate obtained are calculated stoichiometrically. From the P_2O_5 introduced, 99 % react according to reaction (12). The precipitate obtained after filtration contains 13 % moisture.

It is dried in an air flow dryer with flue gases. For this purpose, material balance of the burning process is elabirated. The fuel used is natural gas.

Reactions of burning:

$$CH_4 + 2O_2 = CO_2 + 2H_2O \qquad (16)$$
$$C_2H_6 + 3.5O_2 = 2CO_2 + 3H_2O \qquad (17)$$
$$C_3H_8 + 5O_2 = 3CO_2 + 4H_2O \qquad (18)$$
$$C_4H_{10} + 6.5O_2 = 4CO_2 + 5H_2O \qquad (19)$$
$$C_5H_{12} + 8O_2 = 5CO_2 + 6H_2O \qquad (20)$$
$$C_6H_{14} + 9.5O_2 = 6CO_2 + 7H_2O \qquad (21)$$

The calculations are carried out at burning air excess $\alpha = 1.15$ and relative humidity of air $\varphi = 75$ %.

The quantities of the components in the air and in the flue gas produced are determined. As the flue gas leaving the burner has temperature as high as $1200^0 - 1300\ ^0C$ while the drying should be carried out at 70-80 ^0C, additional air flow is required to decrease the flue gas temperature to 213 ^0C. The amount of secondary air introduced in the mixer is determined from the heat balance of the mixer.

The moisture content in the end product should be maximum 3 %. The total efficiency of the cyclones and the sleeve filter is about 99.88 %. The allowable dust content in the gas releases in the atmosphere is 150 mg/m³[4,18]. The product loss is about 0.12 % of the theoretical amount of dry dicalcuim phosphate dihydrate which should be obtained.

For the formation of the heat balance, all physical heats of the inflows and outflows, as well as the heat effects of the chemical reactions taking place in the apparatuses are taken into account. The physical heats ($Q_{ph\ heat}$) are calculated using the formula[19].

$$Q_{ph\ heat} = C_p.t.G \qquad (22)$$

where C_p is the isobaric specific heat capacity of the material flow in kJ/kg; t is the working temperature in the flow, K;G is the rate of the material flow, kg/h.

The material flows are regarded as ideal mixtures of individual substances since the processes in the production studied occur at atmospheric pressure[19]. Their isobaric specific heat capacity is calculated by summing the isobaric specific heat capacities of the components present in the flow. The heat effects of the reactions are determined by the Hess's law at T=298 K from the standard heats of the formation of the products and the initial substances taking part in the reactions[19,20]:

$$\Delta_r H^0_{reaction} = \Sigma\Delta_f H^0_{products} - \Sigma\Delta_f H^0_{input\ compounds} \qquad (23)$$

where $\Delta_f H^0_{reaction}$ – heat of the reaction, kJ/mol; $\Sigma\Delta_f H^0_{products}$ – sum of the heat capacities of the end products, kJ/mol (standard enthalpy of formation); $\Sigma\Delta_f H^0_{input\ compounds}$ – sum of the heats of formation of the initial substances, kJ/mol (standard enthalpy of formation)

The heat released by the burning of natural gas is calculated from the heats of the burning of its components[21].

The heat losses are calculated as the difference between the heat introduced in the system and the heat carried out of the system.

EXERGY BALANCE

Based on the material and heat balances calculated, the exergy balances of the whole production line of dicalcium phosphate dihydrate and the individual stages are made (TABLES 2- 12). For this purpose, the exergies of the main materials and energy flows are preliminarily calculated for the system[5,6,22]. Each material flow taking part in the processes studied consists of a number of individual substances. Some of the material flows are in gaseous phase, others are fluid or solid. All the material flows studied are at atmospheric pressure. Therefore, the exergy of each phase is considered to be the exergy of an ideal mixture of individual substances. The exergy of each material flow is calculated as the sum of its physical and chemical exergy and the exergy of mixing (TABLE 1):

$$e_{ex} = e_{ex}^{PH} + e_{ex}^{CH} + e_{ex}^{mixing} \qquad (24)$$
$$e_{ex}^{PH} = (h - h_0) - T_0(s - s_0) \qquad (25)$$

where h and s are the enthalpy and entropy of the material flow at its working parameters (temperature, pressure and composition), respectively, while h_0 and s_0 –

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the enthalpy and entropy under environmental conditions, $T_0 = 298.15$ K and $P_0 = 101\ 325$ Pa.

The enthalpy and entropy of a mixture of substances are calculated by summing the enthalpies and entropies of the individual substances present in the mixture. The values of the individual enthalpies and entropies are taken from reference literature[19,20,23-26]. The chemical exergy is calculated using the method of Szargut described in[22].

The exergy of mixing is calculated by the formula:

$$E_{ex}^{mixing} = -RT_0 \Sigma x_i ln x_i \qquad (26)$$

where R is the universal gas constant, T_0 is the environmental temperature (298.15 K) and x_i is the mole fraction of the ith component of the mixture.

The dead state conditions in all the calculations were: temperature $T_0 = 298.15$ K, pressure $P_0 = 101\ 325$ Pa and composition $x_0 = $ Szargut model[22].

The inflowing exergy is calculated as the sum of the exergies of all the incoming flows in the system analyzed: E_{in}. The outflowing exergy is calculated as the sum of all the useful flows that leave the system: E_{out}. The difference between inflowing and outflowing exergy streams is the net exergy loss, D:

$$D = E_{in} - E_{out} \qquad (27)$$

The total exergy losses are apportioned to internal and external regions. The external exergy losses are the sum of the exergies of material and energy flows that are discharged in the environment without further utilization, D_{ext}. The internal exergy losses D_{int} are determined as the difference between the total and the external exergy losses:

$$D_{int} = D - D_{ext} \qquad (28)$$

The exergy efficiency η_e is determined as the ratio of outflowing to inflowing exergy[5,22].

$$\eta_e = E_{out}/E_{in} \qquad (29)$$

DISCUSSION ON THE RESULTS

The exergy efficiency calculated (h_e) for the whole production of dicalcium phosphate dihydrate is 2.33 % (TABLE 2).

The values obtained shows that the production of dicalcium phosphate dihydrate obtained by decomposition of natural phosphate material with hydrochloric acid is thermodynamically imperfect.

The total exergy losses of the process studied are quite high (9692.59 MJ/t product) and 36.61 % of them

TABLE 2 : Exergy balance of the process of the dicalcium phosphate dihidrate production

Number, Flows	Input exergy, MJ.t⁻¹ product	Number, Flows	Output exergy, MJ.t⁻¹ product
1. Hydrochloric acid	2825.06	28. Product-precipitate	230.96
2,8,15. Water	1298.36	Useful exergy	230.96
4. Phosphate rock	3173.69	External exergy losses from the material flows:	3254.08
7,14. Limestone	78.27	5. Gas	127.64
23,25. Air	0.00	10. Gas	2.21
22. Natural gas	2171.56	12. Sediment	779.92
Electricity	376.62	17. Gas	112.69
		19. Waste water	2154.20
		29. Gas and dust to the atmosphere	77.42
		External exergy losses from the heat losses	294.07
		Internal exergy losses	6144.44
		Total exergy losses	9692.59
Total	9923.55	Total	9923.55

Exergy Efficiency = 0.0233

are due to the external exergy losses while the other 63.39 % are due to internal exergy losses (TABLE 2 and Figure 2).

It can be seen from the total exergy balance of the production of dicalcium phosphate dihydrate (TABLE 2 and Figure 3) that the highest exergies are observed for the exergies of the inflowing hydrochloric acid with concentration of 33 mass %, the rock phosphate (phos-
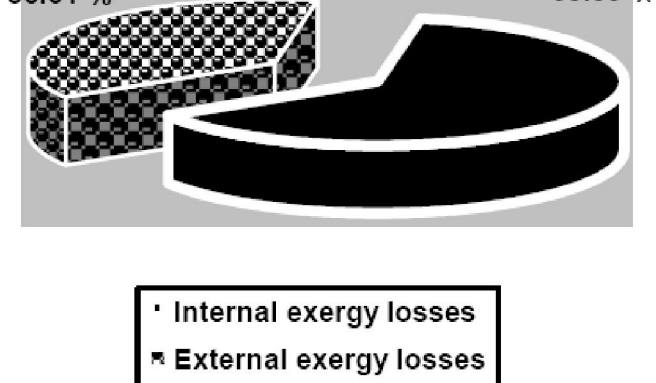
36.61 %   63.39 %

· Internal exergy losses

▪ External exergy losses

Figure 2 : External and internal exergy losses in the production line for dicalcium phosphate dihydrate as per cent of the total exergy losses

phorite), fresh water and the natural gas. At the same time, the exergy of the product obtained is low. This results in low exergy efficiency of the whole process (2.33 %).
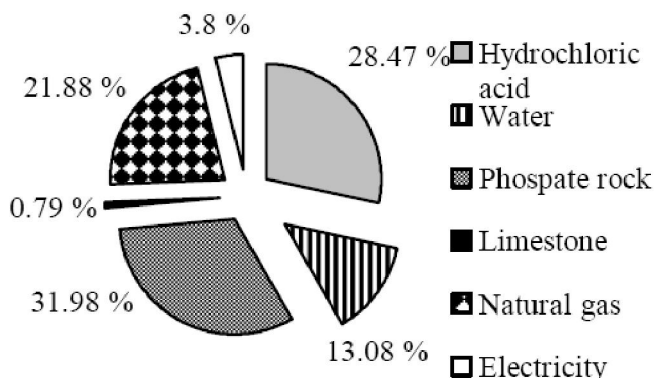

Figure 3 : Distribution of the exergies of the inflows by the production of precipitaste as percent of the inlet exergy

The value of the external exergy losses with material flows which remain unused but are dumped into the environment is also high (Figure 4 and TABLE 2). The comprise 91.71 % (3254.08 MJ/t product) of all the external exergy losses.
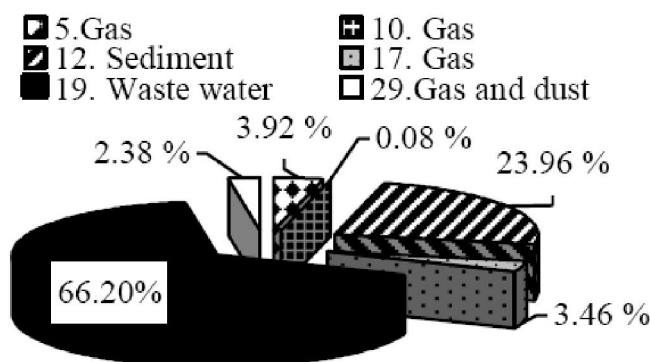

Figure 4 : Distribution of the external exergy losses from the material flows as per cent of the total exergy losses with material flows

The waste water from the centrifuges has high exergy (66.2 % of all the external exergy losses with the material flows), as well as the sediment at filter-press outlet which is 23.96 % of the exergy losses with the material flows. The material balance showed that the sediment contained about 42 % $CaCl_2$, about 24.5 % insoluble residue and about 23 % water (TABLE 1). It can be seen that the sediment carries valuable components as calcium dichloride and about 10 % P_2O_5 which is present in the insoluble residue since its degree of extraction from the initial phosphorite is 90 %. From the

initial raw materials, phosphorite and hydrochloric acid, phosphoric acid is obtained which is further used in the process for the production of the goal product precipitate but, simultaneously, calcium dichloride is produced which is discharged as waste material. Therefore, exergy is introduced with the phosphorite and hydrochloric acid and part of it is used to obtain phosphoric acid necessary for the main process but the other part of the exergy introduced is used for generation of the waste product $CaCl_2$. About 66 % of the exergy losses with the material flows are due to the waste water from the centrifuges containing about 7 % $CaCl_2$ (Figure 4).

Smaller part of the external exergy losses are due to the gaseous phases released in the atmosphere from Reactors I and II, Section "Reaction" and dust emissions in the atmosphere. The highest portion of the external exergy loses from the heat losses (237.95 MJ/t product) is generated in the "Drying" section (Figure 5 and TABLE 9).

The internal exergy losses are mainly due to the irreversibility of the reactions taking place in Reactor I (45.8 % of all the internal losses in the system), in sec-
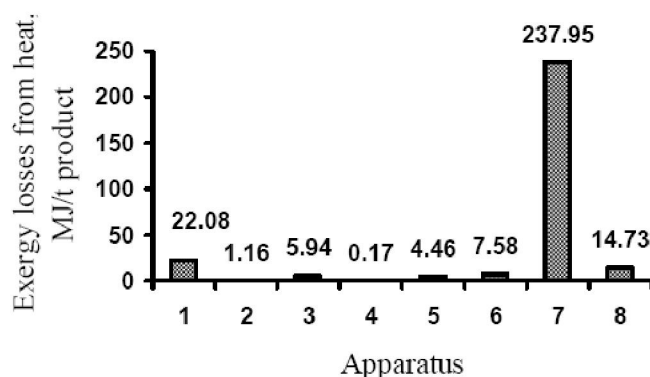

Figure 5: External exergy losses from the heat losses in individual apparatuses of precipitate production.

1- Reactor I, 2- Reactor II, 3 – Filter-press, 4- Section "Reaction", 5- Section "Filtration", 6- Burner and Mixer, 7- Air flow dryer, 8- Cyclones and Filter

tion "Reaction" where precipitate is produced (13.8 %) and in the burning chamber where fuel burns (28.04 %), (TABLES 3-10, Figure 6). These reactions cannot be avoided.

From thermodynamic point of view, the direct heat-exchange and mixing taking place in the air flow dryer and in the mixer of the flue gas with secondary air are ineffective processes (Figure 1). This ineffectiveness is due to the exergy losses of the irreversible process of

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TABLE 3 : Exergy balance of the Reactor I

Number, Flows	Input exergy, MJ.t⁻¹product	Numberp Flows	Output exergy, MJ.t⁻¹ product
3. Hydrochloric acid, 11 %	3881.94	6. Suspension	4105.01
4. Phosphate rock	3173.69	Useful exergy	4105.01
Electricity	82.96	External exergy losses from the material flows:	127.64
		5. Gas	127.64
		External exergy losses from the heat losses	22.08
		Total external exergy losses	149.72
		Internal exergy losses	2883.86
		Total exergy losses	3033.58
Total	7138.59	Total	7138.59

Exergy Efficiency = 0.5750

heat- and mass-exchange between the product and air

TABLE 5 : Exergy balance of the Filtration.

Number, Flows	Input exergy, MJ.t⁻¹product	Number, Flows	Output exergy, MJ.t⁻¹ product
11. Suspension	3988.52	13. Solution of the phosphoric acid	2958.21
Electricity	33.18	Useful exergy	2958.21
		External exergy losses from the material flows:	779.92
		12. Sediment	779.93
		External exergy losses from the heat losses	5.94
		Total external exergy losses	785.87
		Internal exergy losses	277.62
		Total exergy losses	1063.49
Total	4021.70	Total	4021.70

Exergy Efficiency = 0.7356

TABLE 4 : Exergy balance of the Reactor II

Number, Flows	Input exergy, MJ.t⁻¹ product	Number Flows	Output exergy, MJ.t⁻¹ product
6. Suspension	4105.01	11. Suspension	3988.52
9. Suspension of $CaCO_3$, 22 %	8.10	Useful exergy	3988.52
Electricity	49.77	External exergy losses from the material flows:	2.20
		10. Gas	2.20
		External exergy losses from the heat losses	1.16
		Total external exergy losses	3.36
		Internal exergy losses	171.00
		Total exergy losses	174.36
Total	4162.88	Total	4162.88

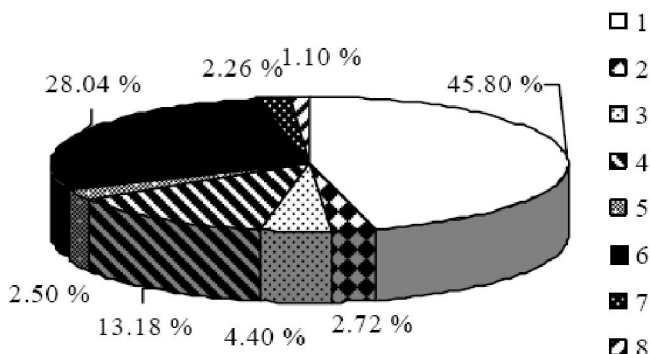**Exergy Efficiency = 0.9581**

Figure 6 : Distribution of the internal exergy losses per apparatus as per cent of all the internal exergy losses in the precipitate production

1- Reactor I, 2-Reactor II, 3- F press, 4- Section "Reaction", 5- Section "Filtration", 6- Burner and Mixer, 7 – Air flow dryer, 8 – Cyclones and Filter.

in the air flow dryer and between flue gas and secondary air in the mixer. The internal exergy losses in these apparatuses are also due to the mixing of material flows with different temperatures. During drying, the wet product with temperature of 40°C is mixed with the flue gas which has temperature of 213 ⁰C (TABLE 1). In the mixer by the burner, flue gas with temperature of 1235 °C is mixed with secondary air which has ambient temperature (TABLE 1).

The flue gas is fed into the drying process at tem-

TABLE 6 : Exergy balance of the Section "Reaction"

Number, Flows	Input xergy, MJ.t^{-1} product	Number Flows	Output exergy, MJ.t^{-1} product
13. Solution of the phosphoric acid	2958.21	18. Suspension	2455.24
16. Suspension of $CaCO_3$- 22 %	414.88	Useful exergy	2455.24
Electricity	24.89	External exergy losses from the material flows:	112.69
		17. Gas	112.69
		External exergy losses from the heat losses	0.17
		Total external exergy losses	112.86
		Internal exergy losses	829.88
		Total exergy losses	942.74
Total	3397.98	Total	3397.98

Exergy Efficiency = 0.7225

TABLE 8 : Exergy balance of the Burner and Mixer

Number, Flows	Input exergy, MJ.t^{-1} product	Number Flows	Output exergy, MJ.t^{-1} product
22. Natural gas	2171.56	26. Mixed flue gas	414.71
23,25. Air	0.00	Useful exergy	414.71
Electricity	16.59	External exergy losses from the heat losses	7.58
		Total external exergy losses	7.58
		Internal exergy losses	1765.86
		Total exergy losses	1773.74
Total	2188.15	Total	2188.15

Exergy Efficiency = 0.1895

perature of 213 °C while the product to be dried has temperature of 40 °C. These losses could be reduced

TABLE 7 : Exergy balance of the Section "Filtration"

Number, Flows	Input exergy, MJ.t^{-1} product	Number, Flows	Output exergy, MJ.t^{-1} product
18. Suspension	2455.24	21. Wet product	258.23
Electricity	119.45	Useful exergy	258.23
		External exergy losses from the material flows:	2154.20
		19. Waste water	2154.20
		External exergy losses from the heat losses	4.46
		Total external exergy losses	2158.66
		Internal exergy losses	157.80
		Total exergy losses	2316.46
Total	2574.69	Total	2574.69

Exergy Efficiency = 0.1003

if the product to be dried is fed into the air flow dryer at higher temperature. From technological point of view, however, the product temperature should not exceed 50 °C since the unstable form of calcium phosphate called monetite ($CaHPO_4$) will be obtained. The heat

TABLE 9 : Exergy balance of the Air flow dryer

Number, Flows	Input exergy, MJ.t^{-1} product	Number, Flows	Output exergy, MJ.t^{-1} product
21. Wet product	258.23	27. Flue gas and product	342.74
26. Mixed flue gas	414.71	Useful exergy	342.74
Electricity	49.77	External exergy losses from the heat losses	237.95
		Total external exergy losses	237.95
		Internal exergy losses	142.02
		Total exergy losses	379.97
Total	722.71	Total	722.71

Exergy Efficiency = 0.4742

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TABLE 10 : Exergy balance of the Cyclones and filter

Number, Flows	Input exergy, MJ.t^{-1}product	Number, Flows	Output exergy, MJ.t^{-1} product
27. Flue gas and product	342.74	28. Product - precipitate	230.96
Electricity	49.77	Useful exergy	230.96
		External exergy losses from the material flows	77.42
		29. Gas and dust to the atmosphere	77.42
		External exergy losses from the heat losses	14.73
		Total external exergy losses	92.15
		Internal exergy losses	69.40
		Total exergy losses	161.55
Total	392.51	Total	392.51

Exergy Efficiency = 0.5884

of the reaction by which dicalcium phosphate dihydrate is obtained allows increasing its temperature up to 40 °C. To increase the temperature further to 50 C, additional heat should be supplied which is inefficient unless there is waste heat which could be utilized.

The lowest exergy efficiency (10.03 %) has section "Filtration" (TABLE 7) since major part of the exergy introduced is dumped into the environment with the waste water. The use of waste water could increase the exergy efficiency of the section up to 93.7 %.

The second lowest exergy efficiency is observed in the subsystem burner-mixer where $h_a = 18.95$ %. Here, the low exergy efficiency is due to the irreversibility of the burning process and the irreversibility of the process of mixing the flue gas with secondary air. The temperature difference between the flows mixed is very high – the flue gas has temperature of 1235 °C while the secondary air has ambient temperature.

It can be seen from the exergy balances made for the subsystem for production of phosphoric acid and the subsystem for neutralization of the phosphoric acid to obtain dicalcium phosphate dihydrate that the latter subsystem has very low exergy efficiency – 4.02 % (TABLES 11-12). There are several reasons for this.

First, the material flows supplied to this system are of very high exergy. The solution of phosphoric acid has exergy of 2958.21 MJ/t product and the exergy of the natural gas is 2171.56 MJ/t product. At the same time, the end product (dicalcium phosphate dihydrate) has low exergy and high internal and external exergy losses. The highest external exergy losses are with the waste water discharged (2154.20 MJ/t product). The internal losses which are found to be 2907.20 MJ/t product are due mainly to the irreversibility of the reactions taking place in section "Reaction", the irreversibility of the burning process in the burner and the irreversibility of the mixing in the mixers and the air flow dryer.

Several suggestion can be made on the basis of the exergy analysis of the dicalcium phosphate dihydrate production which would result in increased exergy efficiency and decreased exergy losses.

1. Part of the waste water after the centrifuges could be used to dilute the hydrochloric acid to 11 % and prepare a suspension containing 22 % $CaCO_3$. For this

TABLE 11 : Exergy balance of the subsystem for production of phosphoric acid

Number, Flows	Input exergy, MJ.t^{-1}product	Number, Flows	Output exergy, MJ.t^{-1} product
1. Hydrochloric acid	2825.06	13. Solution of the phosphoric acid	2958.21
2,8 Water	975.82	Useful exergy	2958.21
4. Phosphate rock	3173.69	External exergy losses from the material flows:	909.77
		5. Gas	127.64
		10. Gas	2.20
		12. Sediment	779.93
7. Limestone	1.50	External exergy losses from the heat losses	29.19
		Total external exergy losses	938.96
		Internal exergy losses	3244.81
Electricity	165.91	Total exergy losses	4183.77
Total	7141.98	Total	7141.98

Exergy Efficiency = 0.4142

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TABLE 12 : Exergy balance of the subsystem for neutralization of the phosphoric acid, production and drying of the precipitate

Number, Flows	Input exergy, MJ.t⁻¹ product	Number Flows	Output exergy, MJ.t⁻¹ product
13. Solution of the phosphoric acid	2958.21	28. Product-precipitate	230.96
14. Limestone	76.77	Useful exergy	230.96
15. Water	322.54	External exergy losses from the material flows:	2344.31
22. Natural gas	2171.56	17. Gas	112.69
23, 25. Air	0.00	19.Waste water	2154.20
		29. Gas and dust to the atmosphere	77.42
		External exergy losses from the heat losses	257.32
		Total external exergy losses	2601.63
		Internal exergy losses	2907.20
Electricity	210.71	Total exergy losses	5508.83
Total	5739.79	Total	5739.79

Exergy Efficiency = 0.0402

purpose, 8031.92 kg/t product waste water are necessary. The total amount of waste water after the process of centrifuging is 9921.36 kg/t product. Thus, the amount of waste water dumped into the environment would decrease to 1889.44 kg/t product. Thos flow would have much lower exergy - 410.25 MJ/t product. Therefore, if part of waste water exergy is used for dilution of the hydrochloric acid and preparation of suspension of calcium carbonate, the input exergy of water is dropped out, the input exergy for the whole production would become 8625.19 MJ/t product while the exergy efficiency would increase to 2.70 %.

2. The sediment after filter press can be used to extract the valuable component it contains – calcium dichloride. Thus, as the sediment exergy would not be carried out of the system since it is utilized, the sediment exergy would be added to the useful exergy of the end product. Therefore, the useful exergy at the outlet would become 1010.88 MJ/t product (230.96+779.92=1010.88 MJ/t product). The exergy efficiency coefficient increases to 11.72 %.

3. After the burning chamber, flue gas of high temperature is obtained but its heat is not used. This heat can be utilized for the preparation of saturated 0, 35 ÌÐà steam for export or for own technological needs. The heat taken from the flue gas by its cooling from 1235 to 213°C is 1153.78 MJ/t product. From it, 537.09 kg/t product steam with exergy of 391.64 MJ/t product can be obtained. In this case, the steam exergy would be added to the useful exergy (1010.88 + 391.64 = 1402.52 ÌJ/t product). The exergy efficiency would increase to 16.26 %.

4. Use rock phosphates of high P_2O_5 content – about 38-40 % instead of 28 % as it is assumed for the calculations. The use of phosphate raw material of higher quality would result in reduced consumption of phosphorite from 1645.94 kg/t product to 1152.16 kg/t product. Thus, the exergy consumption of the main exergy carrier at the input – phosphorite, would decrease by about 30 % to 2221.58 MJ/t product. Besides, the amount of hydrochloric acid required for the decomposition of this amount of phosphorite would also decrease to 1919.35 kg/t product or by 36 % less hydrochloric acid. Then, the exergy of the hydrochloric acid at the input would also decrease to 1808.05 MJ/t product. The exergy at the input of the whole production line would decrease to 6656.07 MJ/t product and the exergy efficiency would increase to 21.07 %.

CONCLUSION

The material, energy and exergy balances of the process of production of dicalcium phosphate dihydrate and its main stages are made. The total, external and internal exergy losses are determined, as well as the exergy efficiency. The process is found to have very low exergy efficiency – 2.33 %. The total exergy losses are high and 36.61 % of them are external while the other 63.39 % are internal losses. The external exergy losses with the material flows is very high – 91.71 % of all the external exergy losses. About 66 % of the exergy

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losses with material flows are due to the waste water from the centrifuges which contains about 7 % of the valuable component $CaCl_2$. The internal exergy losses are mainly due to the irreversibility of the reactions taking place in Reactor I (45.8 % of all the internal exergy losses), in section "Reaction" (13.8 %) and in the burning chamber (28.04 %).

Suggestions were made which would lead to increased exergy efficiency of the production line studied.:

1. Part of the waste water after the centrifuges van be used for dilution of the hydrochloric acid to 11% and preparation of a suspension containing 22 % $CaCO_3$. Thus, the exergy efficiency increases to 2.70 %.

2. The filtrate after the filter press can be used to extract the valuable component it carries – calcium dichloride. The exergy efficiency increases to 11.72 %.

3. After the burning chamber, high temperature flue gas is generated but its heat remains unused. This heat could be utilized for production of saturated 0, 35 ÌÐà steam in quantity of 537.09 kg/t product which can further be exported or used for own technological needs. The exergy efficiency increases to 16.26 %.

4. Natural phosphates of higher P_2O_5 content (38-40 %) should be used instead of 28 % as is assumed for the calculations. Thus, the exergy efficiency would increase to 21.07 %.

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