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EMISSION OF VOLATILE FLUORINE COMPOUNDS FROM PARTIALLY ACIDULATED PHOSPHATE ROCKS PRODUCTION PROCESS

EMISJA LOTNYCH ZWIĄZKÓW FLUORU Z PROCESU OTRZYMYWANIA FOSFORYTÓW CZĘŚCIOWO ROZŁOŻONYCH

Abstract: Emission of volatile fluorine compounds is considered to be the major environmental concern of the phosphate fertilizers manufacturing process. The results of presented studies indicates that the use of PAPR technology as an alternative to conventional superphosphatic fertilizers reduces F⁻ total emission. For the assumed production capacity of 800 Mg/day of PAPR products a decrease in η_{PAPR} value from 1.0 (SSP) to 0.3 causes a reduction in F⁻ by average: 6045 \rightarrow 1675 kg/day and 1545 \rightarrow 506 kg/day for H₂SO₄ and H₃PO₄ respectively as the mineral acids used for acidulation process, while decrease in η_{PAPR} value from 1.0 (SSP) to 0.5 causes a reduction in F⁻ by average: 6045 \rightarrow 1865 kg/day and 1545 \rightarrow 660 kg/day for H₂SO₄ and H₃PO₄, respectively. Reducing the F⁻ content improves environmental and economic profile of the installation, limits the amount of resulting silica, and allow a reduction in off-gas flow intensity, or spraying density.

Keywords: phosphate fertilizers, partially acidulated phosphate rocks (PAPR), volatile fluorine compounds

Introduction

Manufacturing of phosphate fertilizers involves emission of significant amount of gases, which consist particularly of a mixture of HF and SiF₄, causing the problem of acute phytotoxicity near the fertilizer manufacturing plants [1, 2]. Furthermore, the contamination level of fluoride in fertilizer formulations can reach up to 3 % by weight, what may cause the risk of increased concentrations of fluoride in the soil to phytotoxic values at the long-term application (for example SSP application of 10–30 kgP · ha⁻¹ · year⁻¹ cause introduction into the soil of 1–6 kgF · ha⁻¹ · year⁻¹) [3]. It is strictly dependent on

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the method of purification of waste gases collected from the mixer and reaction den, which typically are scrubbed by a two-stage fan system comprising scrubber, a packed absorption column – sprayed with fluosilicic acid solution and water separator cyclone. Moreover, in conventional superphosphatic technology, periodically stored fluosilicic acid, evolved from the absorption unit of fluorinated gases, is recycled to the powder fertilizer production, where is used as a substitute for the phosphate rock acidulation reaction. It concurrently reduces the consumption of sulfuric or phosphoric acid, and the cost of H_2SiF_6 neutralization [4, 5]. However, this loads fertilizer products with additional fluoride amount, generating a risk of accumulation of its toxic levels in crops [6]. PAPR (*Partially Acidulated Phosphate Rock*) technology seems to be a sustainable solution for the production of phosphate fertilizers in terms of these aspects. It is based on the use of portion of stoichiometric amount of sulfuric acid, phosphoric acid or mixtures thereof, required for the complete dissolution of phosphate rock apatitic structure to form a water-soluble $\text{Ca}(\text{H}_2\text{PO}_4)_2$ [7–11]. Given the current economy, it is profitable and at the same time reduces the adverse environmental aspects. The unit which defines fertilizer formulations of PAPR-type is a degree of PAPR stoichiometric norm (η_{PAPR}) expressed as the ratio of amount of mineral acid actually used to the stoichiometric quantity of acid required to fully acidulate a particular phosphate rock to single superphosphate (SSP):

$$\eta_{\text{PAPR}} = \frac{\eta_{\text{min.ac.}}^{\text{a}}}{\eta_{\text{min.ac.}}^{\text{s}}}$$

where: η_{PAPR} – degree of PAPR stoichiometric norm,
 $\eta_{\text{min.ac.}}^{\text{a}}$ – amount of mineral acid actually used in the acidulation process,
 $\eta_{\text{min.ac.}}^{\text{s}}$ – the stoichiometric quantity of acid required to fully acidulate a particular phosphate rock to SSP.

Conventional SSP in this convention reach $\eta_{\text{PAPR}} = 1$. The η_{PAPR} value determines the content of both available and insoluble phosphate forms. Insoluble forms represent mainly unacidulated parts of phosphate rock. After application to the soil, chemical processes and microbial mineralization take place and turn them into a reserve of phosphorus compounds [12].

Materials and methods

Fertilizer preparations of a PAPR-type were obtained in the model-type Atlas apparatus (Syrris Ltd.) consisting of the following units:

- The ellipsoid bottom experimental reaction vessel made of Teflon, developed with working volume of approximately 0.8 dm^3 , equipped with a cover with openings that enabled feeding the batch;
- Mechanically controlled stirrer IKA RW 28 BASIC;

– Volatile fluorine compounds absorption system in an alkaline solution (NaOH 1 M) comprising a laboratory scrubber with a capacity of 500 cm³, in series with a reaction vessel containing 250 cm³ of a solution of an alkali;

– Diaphragm vacuum pump N86KN.18 Laboport[®] combined with absorption system forcing the process gas flow.

Technical specification of applied apparatus and a process parameters (Fig. 1) enabled in a high degree to imitate the unit processes that occur in the technological line to manufacture single superphosphate (SSP).

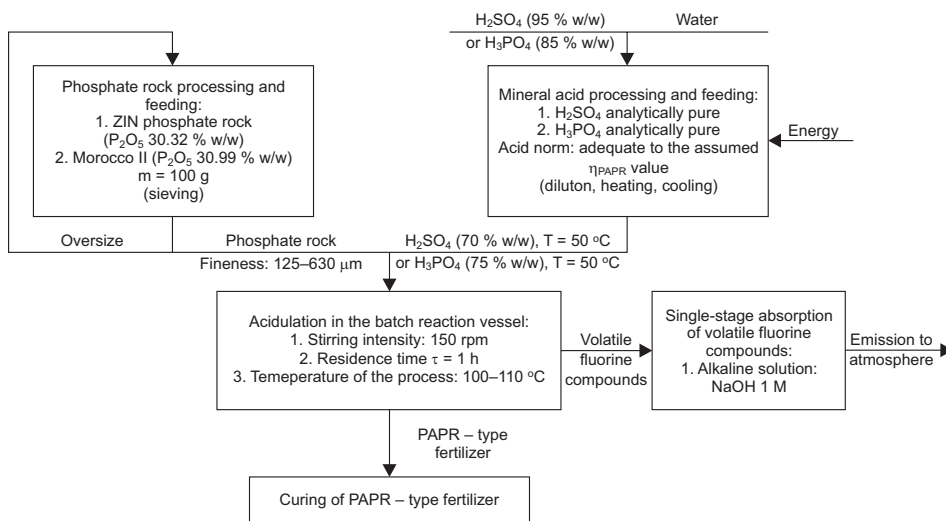


Fig. 1. Schematic diagram of laboratory installation for production of PAPR-type fertilizer formulations

“Morocco II” and “ZIN” phosphate rock samples were used for investigations. The selected raw materials have been widely used by the national phosphate fertilizer manufacturers. Morocco’s enormous measured phosphate rock resources are hosted in upper cretaceous, palaeocene and eocene sediments. Sequences comprising clays, marls, limestones and cherts contain several phosphate-rich beds. Phosphate rock mining centres are operated by Office Chérifien des Phosphates (OCP). Moroccan phosphate rock are enriched by simple mechanical processes [13]. “ZIN” phosphate rocks are being extracted from deposits located in the eastern desert Nagev in Israel. As a commercial product is available in processed form as a result of hydraulic and washing beneficiation [14]. The results of chemical analysis of tested phosphate rocks samples are summarized in Table 1.

The free F⁻ ions content in the investigated samples was determined by potentiometric method using a fluoride ionplus sure-flow solid state combination electrode connected with the multi-parameter laboratory meter 5-STAR (Thermo Scientific Orion). The device allowed the measurement of the concentration of free fluoride ions in range of mg/dm³ against the calibration curve. Calibration of the equipment was

Table 1

Chemical composition of tested phosphate rocks samples

Parameter	Unit	Results for given type of phosphate rock	
		Morocco II	ZIN
P soluble in mineral acids	P ₂ O ₅ % w/w	30.99	30.32
P soluble in 2 % citric acid (20 g per dm ³)	P ₂ O ₅ % w/w	2.02	5.69
P soluble in 2 % formic acid (20 g per dm ³)	P ₂ O ₅ % w/w	1.49	5.52
P soluble in neutral ammonium citrate	P ₂ O ₅ % w/w	2.91	3.66
P water-soluble	P ₂ O ₅ % w/w	insoluble	insoluble
F	% w/w	3.44	3.61
CaO	% w/w	54.80	49.59
Al ₂ O ₃	% w/w	0.12	0.24
Fe ₂ O ₃	% w/w	0.41	0.40

performed based on the measurement of the potential of standard solutions with concentrations of 100, 250 and 500 mg/dm³ F⁻. The procedure for measuring the concentration of F⁻ ions, developed on the basis of Al-Othman's research, was shown schematically in Fig. 2 [17].

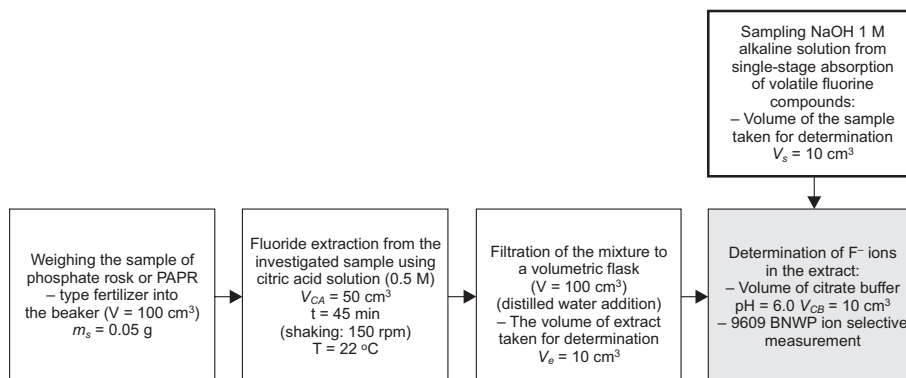


Fig. 2. Schematic diagram of the procedure for determination of the F⁻ ions in the examined samples

Results and discussion

Table 2 depicts the simplified material balance for the absorption of volatile fluorine compounds evolved from the products of Morocco II phosphate rock dissolution using PAPR technique with H₂SO₄. The results were recalculated for an industrial plant with the production capacity of the assumed 800 Mg of PAPR-type fertilizer product per day.

In the course of investigations it was found that the amount of volatile fluorine compounds emitted from the PAPR manufacturing system increases with higher values of η_{PAPR} along. The reference product $\eta_{\text{PAPR}} = 1$ was characterized by the maximum level of emissions of volatile fluorine compounds, revealing the highest absorption

Table 2

A simplified material balance for the process of absorption of the volatile F compounds from the products of Morocco II phosphate rock acidulation by PAPR technique using H₂SO₄

Parameter	Unit	Results for given type of fertilizer product depending on η_{PAPR} value				
		0.1	0.3	0.5	0.7	1.0
Fertilizer output	Mg	800.0				
Phosphate rock (Morocco II) consumption	Mg/day	772.0	699.6	626.8	571.9	509.0
F ⁻ content in phosphate rock	Mg/day	26.6	24.1	21.6	19.7	17.5
F ⁻ content in product	Mg/day	26.1	21.4	18.7	17.8	13.7
F ⁻ total emission	kg/day	480.0	2630.0	2840.0	1910.0	3750.0
F ⁻ organised emission	kg/day	237.4	182.6	188.1	358.0	522.3
F ⁻ unorganised emission	kg/day	242.6	2447.4	2651.9	1552.0	3227.7
Gas flow rate	Nm ³ /h	0.4	0.4	0.4	0.4	0.4
Absorption performance	%	52.8	50.8	59.7	78.9	86.3
F ⁻ removal	kg/day	125.4	92.7	112.2	282.5	450.5
Waste F ⁻ emission	kg/day	111.9	89.9	75.8	75.5	71.8

performance and concurrently the lowest F⁻ content in the fertilizer product. Analysis of the absorption performance results for the mixture of HF and SiF₄ showed a declining trend with decreasing values of η_{PAPR} in the laboratory conditions. This may be caused by too low flow rate of exhaust gases which achieves the optimum value of approximately 30000 Nm³/h in an industrial conditions. The rapid growth of emissions of volatile fluorine compounds was observed for fertilizer products of $\eta_{\text{PAPR}} > 0.5$. Table 3 depicts the simplified material balance for the absorption of volatile fluorine compounds evolved from the products of ZIN phosphate rock dissolution using PAPR technique with H₂SO₄.

Table 3

A simplified material balance for the process of absorption of the volatile fluorine compounds from the products of ZIN phosphate rock acidulation by PAPR technique using H₂SO₄

Parameter	Unit	Results for given type of fertilizer product depending on η_{PAPR} value				
		0.1	0.3	0.5	0.7	1.0
Fertilizer output	Mg	800.0				
Phosphate rock (ZIN) consumption	Mg/day	774.1	693.7	636.2	583.2	516.9
F ⁻ content in phosphate rock	Mg/day	27.9	25.0	22.9	21.1	18.7
F ⁻ content in product	Mg/day	27.3	24.3	22.1	18.5	10.3
F ⁻ total emission	kg/day	670.0	720.0	890.0	2570.0	8340.0
F ⁻ organised emission	kg/day	195.5	174.1	156.2	169.4	550.0
F ⁻ unorganised emission	kg/day	474.5	545.9	733.8	2400.6	7790.0
Gas flow rate	Nm ³ /h	0.4	0.4	0.4	0.4	0.4
Absorption performance	%	55.6	54.8	53.4	60.1	87.4
F ⁻ removal	kg/day	108.8	95.4	83.3	101.8	480.7
Waste F ⁻ emission	kg/day	86.7	78.7	72.8	67.7	69.3

A comparison of material balances of volatile fluorine compounds for both phosphate rocks made us able to observe that the F^- content in PAPR-type fertilizer products acidulated with H_2SO_4 of η_{PAPR} values in range of 0.1–0.7 were higher for ZIN phosphate rock sample. This correlates with the higher content of F^- in the raw mineral of approximately 0.5 % w/w against Morocco II phosphate rock. Waste F^- emission values were lower by 5–15 % when ZIN phosphate rock was applied for the dissolution process, particularly for fertilizer products of η_{PAPR} values in range of 0.1–0.5. Other parameters indicated comparable values.

In order to determine the influence of the type of mineral acid applied in the acidulation process (H_2SO_4 or H_3PO_4 in this case) on F^- emission profile, the PAPR-type fertilizers were also manufactured using H_3PO_4 . It was crucial to determine whether there is resemblance in F^- content trends in the particular range of the η_{PAPR} values of PAPR products obtained in the laboratory conditions. Table 4 depicts the simplified material balance for the absorption of volatile fluorine compounds evolved from the products of Morocco II phosphate rock dissolution using PAPR technique with H_3PO_4 .

Table 4

A simplified material balance for the process of absorption of the volatile F compounds from the products of Morocco II phosphate rock acidulation by PAPR technique using H_3PO_4

Parameter	Unit	Results for given type of fertilizer product depending on η_{PAPR} value				
		0.1	0.3	0.5	0.7	1.0
Fertilizer output	Mg	800.0				
Phosphate rock (Morocco II) consumption	Mg/day	727.8	583.4	528.9	431.3	359.7
F^- content in phosphate rock	Mg/day	25.0	20.1	18.2	14.8	12.4
F^- content in product	Mg/day	24.6	19.8	17.9	14.2	10.7
F^- total emission	kg/day	480.0	230.0	280.0	680.0	1660.0
F^- organised emission	kg/day	268.6	178.2	116.1	90.1	79.5
F^- unorganised emission	kg/day	211.4	51.8	163.9	589.9	1580.5
Gas flow rate	Nm ³ /h	0.4	0.4	0.4	0.4	0.4
Absorption performance	%	71.5	64.6	51.0	50.7	52.5
F^- removal	kg/day	192.2	114.3	59.2	45.7	41.7
Waste F^- emission	kg/day	76.4	63.9	56.9	44.4	37.8

Potentiometric analysis for fluoride content determination revealed that the amount of volatile fluorine compounds emitted from the laboratory PAPR manufacturing system based on H_3PO_4 increases with higher values of η_{PAPR} along, likewise in PAPR products acidulated with H_2SO_4 . Moreover, the reference product $\eta_{PAPR} = 1$ was characterized by the maximum level of emissions of volatile fluorine compounds and concurrently the lowest F^- content in the fertilizer product. However, unlike PAPR product acidulated with H_2SO_4 , it had the lowest absorption performance result for the

mixture of HF and SiF₄ while indicating an upward trend with decreasing values of η_{PAPR} in the laboratory conditions. Table 5 depicts the simplified material balance for the absorption of volatile fluorine compounds evolved from the products of ZIN phosphate rock dissolution using PAPR technique with H₃PO₄.

Table 5

A simplified material balance for the process of absorption of the volatile fluorine compounds from the products of ZIN phosphate rock acidulation by PAPR technique using H₃PO₄

Parameter	Unit	Results for given type of fertilizer product depending on η_{PAPR} value				
		0.1	0.3	0.5	0.7	1.0
Fertilizer output	Mg	800.0				
Phosphate rock (ZIN) consumption	Mg/day	726.9	603.5	514.0	445.2	376.4
F ⁻ content in phosphate rock	Mg/day	26.2	21.8	18.6	16.1	13.6
F ⁻ content in product	Mg/day	25.5	20.9	17.5	14.9	12.2
F ⁻ total emission	kg/day	720.0	910.0	1040.0	1190.0	1430.0
F ⁻ organised emission	kg/day	153.0	130.7	110.5	98.6	84.7
F ⁻ unorganised emission	kg/day	567.0	779.3	929.5	1091.4	1345.3
Gas flow rate	Nm ³ /h	0.4	0.4	0.4	0.4	0.4
Absorption performance	%	52.5	52.4	50.9	52.1	52.0
F ⁻ removal	kg/day	80.3	68.5	56.3	51.4	44.0
Waste F ⁻ emission	kg/day	72.7	62.2	54.2	47.2	40.7

The F⁻ content in PAPR-type fertilizer products acidulated with H₃PO₄ were higher for ZIN phosphate rock sample in the whole spectrum of η_{PAPR} values, just as in the case of products acidulated with H₂SO₄. Again, it may be correlated with the higher content of F⁻ in the raw mineral of approximately 0.5 % w/w against Morocco II phosphate rock. Waste F⁻ emission values were virtually at the same levels for both phosphate rocks, whereas the average values were significantly lower in comparison with PAPR fertilizer formulations manufactured using H₂SO₄. Other parameters indicated comparable values.

Conclusions

The study indicates that the use of PAPR technology as an alternative to conventional superphosphatic fertilizers reduces F⁻ total emission. For the assumed production capacity of 800 Mg of PAPR fertilizer products per day a decrease in η_{PAPR} value from 1.0 (SSP) to 0.3 causes a reduction in F⁻ by average: 1545 → 506 kg/day and 6045 → 1675 kg/day for H₂SO₄ and H₃PO₄ respectively as the mineral acids used for acidulation process, while decrease in η_{PAPR} value from 1.0 (SSP) to 0.5 causes a reduction in F⁻ by average: 6045 → 1865 kg/day and 1545 → 660 kg/day for H₂SO₄ and H₃PO₄ respectively. The influence of the type of mineral acid applied in the

acidulation process (H_2SO_4 or H_3PO_4 in this case) on F^- emission profile was particularly shown by indicating an upward trend in the absorption performance results for the mixture of HF and SiF_4 with decreasing values of η_{PAPR} for PAPR products acidulated with H_3PO_4 . Furthermore average waste F^- emission values were significantly lower unlike in PAPR fertilizer formulations manufactured by using H_2SO_4 for acidulation process. A reasonable conclusion to draw from these results is that F^- emission is highly dependent on the amount of phosphate rock feed into the manufacturing process. Thus, in case of PAPR products acidulated with H_3PO_4 the amount of volatile fluorine compounds evolved will be lower for particular η_{PAPR} value for the specified mass unit as the part of P_2O_5 is introduced with H_3PO_4 . Despite improvement of environmental protection issues, the lower content of F^- , which leads concurrently to reduce the amount of resulting silica, may allow also a reduction in off-gas flow intensity, or spraying density, which could potentially lead to decrease the cost of purification of 1 m^3 of the off-gas.

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EMISJA LOTNYCH ZWIĄZKÓW FLUORU Z PROCESU OTRZYMYWANIA FOSFORYTÓW CZĘŚCIOWO ROZŁOŻONYCH

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Abstrakt: Emisja lotnych związków fluoru jest uważana za podstawowe zagrożenie środowiskowe procesów wytwarzania nawozów fosforowych. Rezultaty przeprowadzonych badań wskazują, że stosowanie technologii PAPR jako alternatywy dla konwencjonalnych nawozów superfosfatowych, powoduje zmniejszenie emisji całkowitej F^- . Dla założonej zdolności produkcyjnej 800 Mg/dobę produktów nawozowych typu PAPR obniżenie wartości η_{PAPR} z 1,0 (SSP) do 0,3 powoduje redukcję F^- średnio: 6045 \rightarrow 1675 kg/dobę oraz 1545 \rightarrow 506 kg/dobę dla odpowiednio H_2SO_4 i H_3PO_4 jako kwasów mineralnych zastosowanych w procesie roztwarzania; podczas gdy obniżenie wartości η_{PAPR} z 1,0 (SSP) do 0,5 powoduje redukcję F^- średnio: 6045 \rightarrow 1865 kg/dobę oraz 1545 \rightarrow 660 kg/dobę odpowiednio dla H_2SO_4 i H_3PO_4 . Obniżenie zawartości F^- poprawia profil środowiskowy oraz ekonomiczny instalacji, prowadząc jednocześnie do ograniczenia ilości powstającej krzemionki, pozwalając na zmniejszenie natężenia przepływu gazów odlotowych lub gęstości zraszania.

Słowa kluczowe: nawozy fosforowe, fosforyty częściowo rozłożone (PAPR), lotne związki fluoru

