

Enriched Superphosphate and Ammophosphate Fertilizer Based on Washed Dried Phosphorite Concentrate

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Authors' contributions

This work was carried out in collaboration between both authors. Both authors read and approved the final manuscript.

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ABSTRACT

Development of a technology for obtaining enriched superphosphate and ammophosphate by processing washed and dried phosphorite concentrate (WDPC) in a single cycle. The optimal ratio $P_2O_{5WPPA}:H_2SO_{4mh}:P_2O_{5WDPC} = 1:0.28:0.08$ was found, at which the composition and properties of ammophosphate fertilizer are maximally improved and a single phosphorus fertilizer is additionally obtained. It has been established that on the basis of the solid part of the ammophosphate pulp, samples of enriched superphosphate are obtained with the following indicators (wt., %): $P_2O_{5t.} - 30.16-32.01$; $P_2O_{5ac.c.a.} : P_2O_{5t.} = 98.54-100$; $P_2O_{5water\ solubility\ (w.s.)} : P_2O_{5t.} = 54.3-55.5$; N - 5.45-6.04. A sample of ammophosphate contains (wt., %): $P_2O_{5t.} - 52.43-53.31$; $P_2O_{5ac.c.a.} : P_2O_{5t.} = 94.81-96.27$; $P_2O_{5w.s.} : P_2O_{5t.} = 87.41-88.36$; $CaO_t. - 4.01-4.26$; N - 13.65-14.03 and $SO_{3t.} - 4.37-10.74$. Ammophosphate consists of mono- and diammonium phosphate, ammonium sulfate and dicalcium phosphate. Superphosphate also contains activated phosphorite, complex salts and gypsum. The material balance of the process of their production in a single technological cycle has been calculated.

Keywords: *Sulfuric and phosphoric acid; washed dried concentrate; decomposition; ammonization; separation; enriched superphosphate and ammophosphate; chemical and salt compositions and material balance.*

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1. INTRODUCTION

The consumption of phosphoric acid for the production of ammonium phosphates, in particular ammophos, can be reduced if a certain amount of natural phosphate (apatite or phosphorite) is dissolved in the acid supplied for ammonization. The work [1] shows the conditions for obtaining ammophos with a reduced consumption of H_3PO_4 and studied the effect of natural phosphate from the Mazydag deposit (Turkey), containing, %: P_2O_5 – 28,2; CaO – 40.7; MgO – 0.59; Fe_2O_3 – 6.40; Al_2O_3 – 3.0; others - 15.5 for the composition and properties of the finished product.

It has been revealed that partial replacement of phosphoric acid P_2O_5 with natural phosphate P_2O_5 makes it possible to reduce H_3PO_4 consumption by 4-5% in the production ammophos of grade 1 and accordingly reduce the cost of the product, as well as slightly improve its physical and mechanical properties.

This approach makes it possible to use secondary phosphate raw materials in the production of ammophos.

In the 80-90s of the last century, in order to reduce the consumption rates of the acid reagent for the production of 1 ton of P_2O_5 in ammophos and expand the range of concentrated fertilizers, Russia's specialists developed the technology of a new nitrogen-phosphorus fertilizer - ammophosphate, which contains 43% of nutrients [2,3]. Ammophosphate belongs to the class of partially decomposed phosphates. The process of its production is based on decomposition of natural phosphates by a high rate of H_3PO_4 (150-200% of stoichiometry), followed by neutralization of acidity with ammonia, granulation and drying of the product [2]. The phosphate component of ammophosphate is monoammonium phosphate, and as impurities, dicalcium phosphate and basic calcium phosphates such as hydroxylfluorapatite and unreacted phosphorites, as well as complex salts that fall into the solid phase when ammonizing excess wet process phosphoric acid (WPPC).

In this case, a list of chemical compounds can be provided, the formation of which is possible during ammonia neutralization of extraction phosphoric acids with different composition and content of impurities [3-6]. Thus, in the range pH = 2.5-5.5, the following compounds are formed:

$NH_4H_2PO_4$; $(NH_4)_2SO_4$; $MgHPO_4$;
 $MgNH_4PO_4 \cdot H_2O$; $Mg(Fe,Al)(NH_4)_2(HPO_4)_2F_3$;
 $Mg_3(NH_4)_2(HPO_4)_4 \cdot 8H_2O$; $MgNH_4HFPO_4$;
 $(Fe,Al)NH_4(HPO_4)_2 \cdot 0.5H_2O$; $(Fe,Al)NH_4HPO_4F_2$;
 SiO_2 ; $CaHPO_4$; $Ca_5(PO_4)_3OH$. All phosphates are citrate soluble except hydroxylapatite.

Neutralization of WPPC in the presence of ammonium fluoride or silicofluoride can lead to the formation of a number of fluorides Fe, Al, Ca, Mg. In the absence of ammonium fluorides and silicofluorides, hydroxides are formed. They are significantly degrade the quality of the finished product.

In order for improve the quality of ammophosphate, that is, to increase the content of total (t.) and water soluble(w.s.) phosphorus in it, it is necessary to clean the pulp from solid suspensions, magnesium compounds and one and a half oxides (Fe_2O_3 , Al_2O_3 and others).

This can be accomplished by separating the ammophosphate pulp into solid and liquid phases. The solid phase is nothing more than concentrated enriched superphosphate, and the liquid phase after preammonization, granulation and drying is high-quality ammophosphate.

The essence of this process is the decomposition of phosphate raw materials with phosphoric acid; separation of acid phosphate pulp into liquid and solid phases; granulation and drying of the solid phase by pelleting to obtain a single phosphorus fertilizer such as enriched superphosphate; ammonization of the liquid phase with ammonia to pH = 4.0-4.5 followed by granulation and drying of the product on cylinder granulator drier (CGD) with obtaining a nitrogen-phosphorus fertilizer such as ammophosphate.

This approach is made in [7], where two different types of product are obtained in one cycle. This work uses mineralized mass (MM - 14.33% P_2O_5) and WPPC with a content of 14.32% in the range of weight ratios $P_2O_{5WPPC} : P_2O_{5MM}$ from 1: 0.38 to 1: 0.165. It is shown that after separation of phosphate acid-phosphate pulp and drying its solid part, enriched superphosphate of the composition (wt., %) was obtained: 30.57-32.53 P_2O_{5t} ; 26.78-31.02 CaO_t ; $P_2O_{5ac.c.a.} : P_2O_{5t} = 59.42-65.14$; $P_2O_{5w.s.} : P_2O_{5t} = 13.54-36.30$ and $CaO_{ac.c.a.} : CaO_t = 41.38-47.45\%$ and on the basis of the liquid part of the pulp after its ammonization to 4.5 and drying, an ammophosphate was obtained, containing (wt., %): N from 6.54 to 9.12%; P_2O_{5t} from 47.62 to

50.38%; CaO_t from 12.72 to 16.99%; $\text{P}_2\text{O}_{5\text{ac.c.a.}}$: P_2O_{5t} from 98.64 to 100%; $\text{P}_2\text{O}_{5\text{w.s.}}$: P_2O_{5t} from 54.30 to 66.82%; $\text{CaO}_{\text{w.s.}}$: CaO_t from 99.13 to 100%.

In these articles [8,9] obtained complex nitrogen-phosphate fertilizers based on activation of phosphorite powder with partially ammoniated mix of phosphoric and sulphuric acids and also a mixture of phosphoric and sulphuric acids have been studied. In order to reduce the foaming of the process, for the first time a partially ammoniated mix of acids was used. The optimal technological parameters for activation phosphorite powder with partially neutralized mixes of sulphuric and phosphoric acids are the followings: the mix of sulphuric and phosphoric acids with a ratio of $\text{SO}_3:\text{P}_2\text{O}_5 = 1.2$; pH of acids – 2.5; weight ratio of ammonium sulphate-phosphate slurry towards phosphorite powder is 100 : 20; temperature is 60°C; duration is 30 min. The composition nitrogen-phosphate fertilizers obtained in optimal condition contains (wt., %): N – 11.55; P_2O_{5t} - 24.61; $\text{P}_2\text{O}_{5\text{ac.c.a.}}$ -21.66; $\text{P}_2\text{O}_{5\text{w.s.}}$ -13.02; CaO_t - 13.59; $\text{CaO}_{\text{ac.c.a.}}$ -11.43. In that condition, granulated products of nitrogen-phosphate can be produced with high strength. The advantage of offered promising technology concludes in reduction two times expenditure of the most expensive ammonia in comparison with ammonium sulphate production and an increase in gross domestic product.

However, the enriched superphosphate contains only $\text{P}_2\text{O}_{5\text{ac.c.a.}}$: $\text{P}_2\text{O}_{5t} = 59.42\text{-}65.14\%$ and $\text{P}_2\text{O}_{5\text{w.s.}}$: $\text{P}_2\text{O}_{5t} = 13.54\text{-}36.30\%$, which does not support their agrochemical effectiveness. At the request of agriculture, phosphorus containing fertilizer should have a high content of the total and acceptable forms of P_2O_5 , and the ratio of $\text{P}_2\text{O}_{5\text{w.s.}}$: P_2O_{5t} must be at least 50%. For example, the composition of the products of «DAGFOS» OJSC (Russia) - enriched superphosphate contained (wt., %): P_2O_{5t} at least 29%; $\text{P}_2\text{O}_{5\text{ac.c.a.}}$: P_2O_{5t} not less than 90%; $\text{P}_2\text{O}_{5\text{w.s.}}$: P_2O_{5t} at least 50%.

The purpose of this research work is to obtain high-quality ammophosphate and enriched superphosphate from low grade phosphate raw materials.

2. METHODS AND MATERIALS

In our works [10-12], we studied the process of producing enriched superphosphate and

ammophosphate using the example of washed dried phosphorite concentrate (WDPC) - phosphorite products used to obtain washed and burned concentrate. It contains (wt., %): 26.08 P_2O_5 ; $\text{P}_2\text{O}_{5\text{ac.c.a.}}$: $\text{P}_2\text{O}_{5t} = 13.11$; 51.74 CaO; 0.89 MgO; 0.31 Fe_2O_3 ; 1.02 Al_2O_3 ; 1.59 SO_3 ; 9.95 CO_2 ; 3.41 F; 2.51 insoluble reduce (i.r.). For its decomposition was used WPPA contained (wt, %): 7.92 P_2O_5 ; 0.21 CaO; 0.30 MgO; 0.56 Al_2O_3 ; 0.45 Fe_2O_3 ; 1.83 SO_{3t} ; 1.53 $\text{SO}_{3\text{free}}$ and 93.5% sulfuric acid.

The addition of WDPC to WPPA is explained by the fact that pure phosphoric acid decomposition does not provide the maximum development of the phosphate mineral. Decomposition of WDPC was performed at mass ratio of $\text{P}_2\text{O}_{5\text{WPPA}}$: $\text{H}_2\text{SO}_{4\text{mh}}$: $\text{P}_2\text{O}_{5\text{WDPC}}$ from 1: 0.11: 0.12 to 1: 0.28: 0.12 at 70°C for 60 minutes.

Before filtration, phosphoric acid gypsum slurries (PAGS) were ammonized to pH = 1.6; 2.0; 2.5 and 3.0. Then they were separated into liquid and solid phases by vacuum filtration. The residue remaining on the filter was dried. The filtrate, i.e. the liquid phase, was further ammonized to pH = 5 and dried. Granulation of products, obtained from the solid phase and the liquid phase was carried out during the drying process by method of pelleting.

The products were subjected by conventional procedures [13]. Form of N total (t) was determined by method Kjeldahl's nitrogen [14]. The acceptable forms of P_2O_5 and CaO were determined by citric acid, the pH of the pulp was measured by laboratory ion meter I-130M.

In this work, X-ray analysis was performed on a XRD-6100 diffract meter (Shimadzu, Japan) to determine the salt composition of both products. $\text{CuK}\alpha$ emission (β filter, Ni, tube current and voltage mode 30 mA, 30 kV) and constant detector rotation speed 4 deg/min were used, and the scanning angle varied from 4 to 80°. The interpretation and identification of mineral phases was carried out using catalogs [15, 16].

3. RESULTS AND DISCUSSION

The results of chemical analysis established that the optimal ratio of $\text{P}_2\text{O}_{5\text{WPPA}}$: $\text{H}_2\text{SO}_{4\text{mh}}$: $\text{P}_2\text{O}_{5\text{WDPC}}$ 1: 0.28: 0.08 can be considered and the pulp pH is 2.5-3. At the same time, samples of enriched superphosphate are obtained on the basis of the solid part of the pulp with the following parameters (wt., %): P_2O_{5t} - 30.16-32.01;

$P_2O_{5ac.c.a.}$: $P_2O_{5t.}$ = 98.54-100; $P_2O_{5w.s.}$: $P_2O_{5t.}$ = 54.3-55.5; N - 5.45-6.04 and quite suitable as an effective phosphorus fertilizer for a ploughed land.

Under the conditions found from the liquid part after its extra ammonization (pH = 5), the obtained ammophosphate fertilizers have (wt., %): $P_2O_{5t.}$ - 52.43-53.31; $P_2O_{5ac.c.a.}$: $P_2O_{5t.}$ = 94.81-96.27; $P_2O_{5w.s.}$: $P_2O_{5t.}$ = 87.41-88.36; CaO_t - 4.01-4.26; $CaO_{ac.c.a.}$ - 3.74-3.87; N - 13.65-14.03 and $SO_{3t.}$ - 4.37-10.74. The latter component represents a water soluble $(NH_4)_2SO_4$ and calcium represents a citrate-soluble $CaHPO_4$.

Balakhovo production association (PA) "Minudobreniya" in Russia produces ammonium phosphate of the highest brand A. Its composition (mass., %): N 9.78; $P_2O_{5t.}$ 50.25; $P_2O_{5ac.c.a.}$ 47.60; $P_2O_{5w.s.}$ 40.0. The quality of the ammophosphate fertilizers we obtain is not inferior to it, and in some parameters they are even superior.

Fig. 1 shows an X-ray pattern of enriched superphosphate obtained at the ratio P_2O_{5WPPA} : $H_2SO_{4mh.}$: P_2O_{5WDPC} = 1 : 0.28 : 0.08. Analyzing the roentgenograms, it can be concluded that the dried solid phase consists of monoammonium phosphate (5.29; 3.73; 3.06; 2.64; 2.00 Å), monocalcium phosphate (4.92; 2.85 Å), dicalcium phosphate (3.38 Å), activated fluorocarbonate apatite (3.48; 3.17; 2.76; 2.71; 1.84 Å) and gypsum of different forms (6.29; 6.00; 3.01; 2.80 Å).

The phase composition of the ammonium phosphate fertilizer (Fig. 2) is represented by monoammonium phosphate (5.30; 3.74; 3.06; 2.65; 2.00 Å), diammonium phosphate (5.20 Å), dicalcium phosphate (4.32 Å), ammonium sulfate (5.38; 4.32-4.38; 2.36 Å). At the same time, lanes 5.30; 3.06; 2.65 Å refers to both sulfate and ammonium phosphate.

Based on laboratory experiments, the material balance of enriched superphosphate and concentrated ammophosphate in a single technological cycle is calculated (Fig. 3).

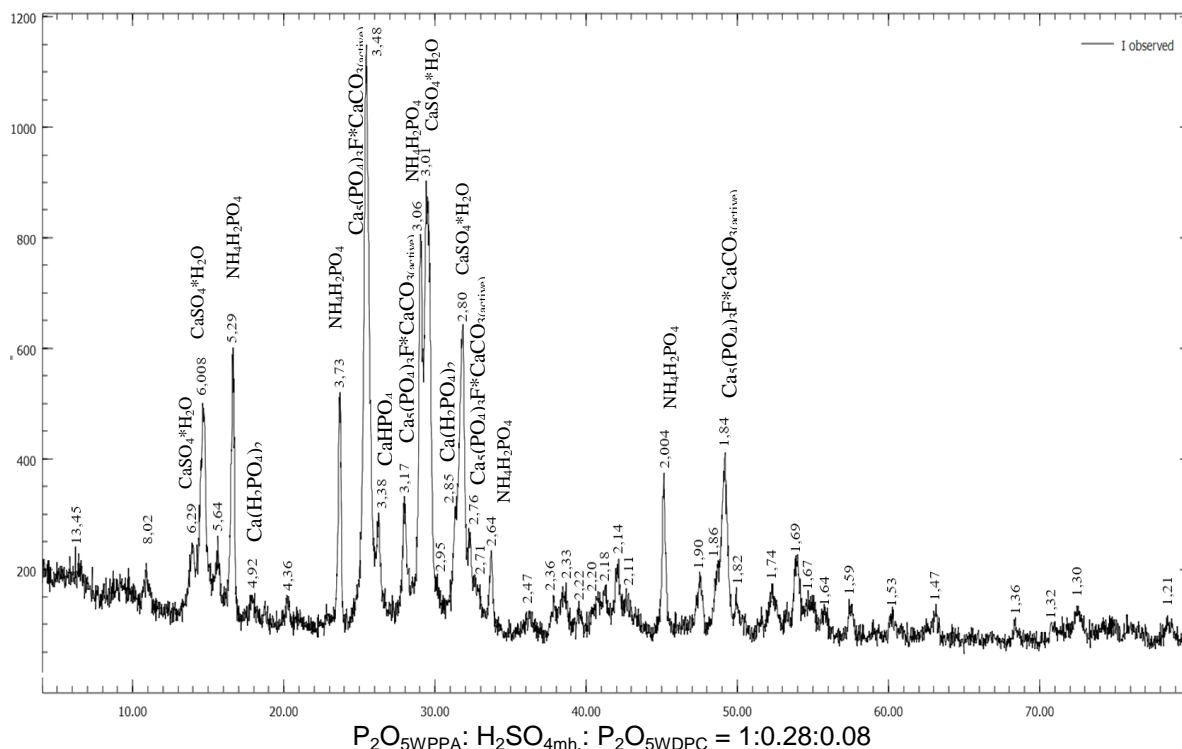
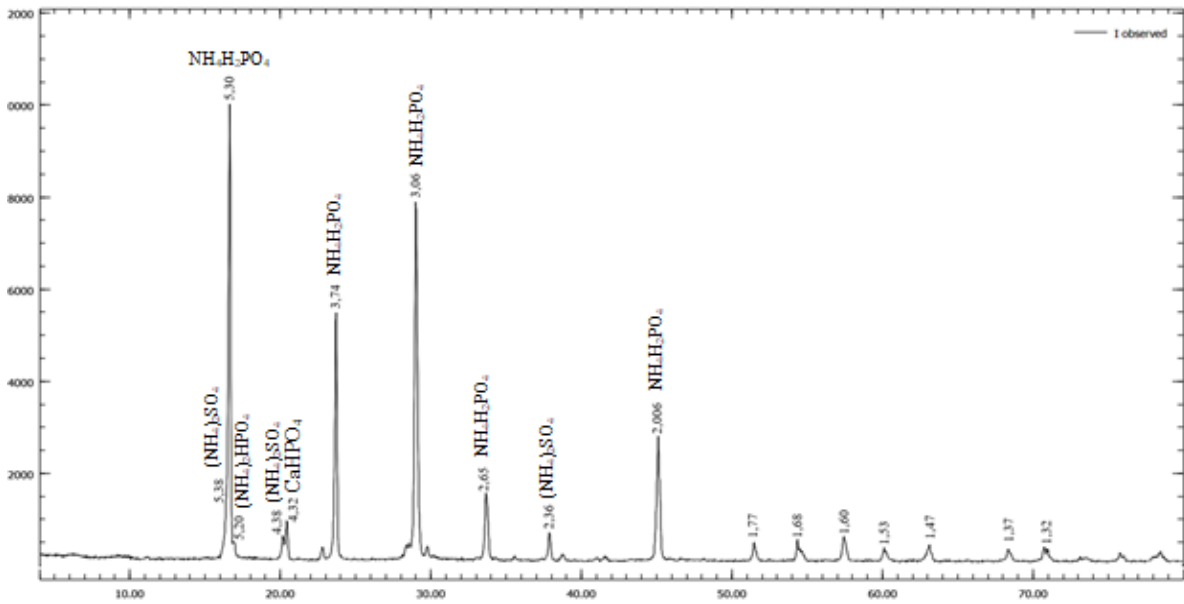


Fig. 1. Radiograph of enriched superphosphate on base solid part of ammophosphate pulp



$P_2O_{5WPPA} : H_2SO_{4mh.} : P_2O_{5WDPC} = 1 : 0.28 : 0.08$

Fig. 2. Radiograph of concentrated ammophosphate fertilizer based on liquid part of ammophosphate pulp

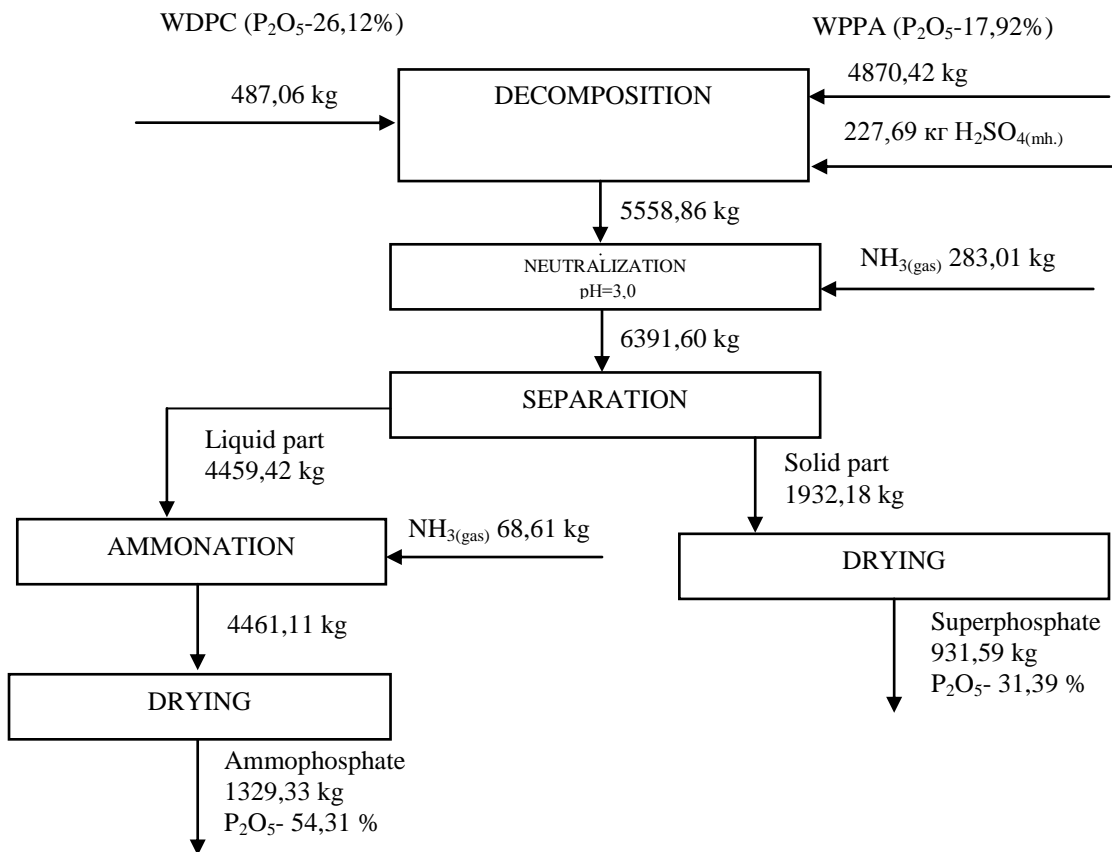


Fig. 3. The material balance of enriched superphosphate and concentrated ammophosphate in a single technological cycle

4. CONCLUSION

The process of obtaining concentrated grades of enriched superphosphate and ammophosphate by separating phosphorus-sulfur acid decomposition products of washed dried concentrate into solid and liquid phases has been studied. The optimal ratio of P_2O_{5WPPA} : H_2SO_{4mh} : P_2O_{5WDPC} is 1: 0.28: 0.08 and the pulp pH is 2.5-3. X-ray research of both dried phases was performed. The solid phase is represented by mono- and diammonium phosphates, mono- and dicalcium phosphates, activated phosphorite and gypsum. The dried ammophosphate mainly contains mono- and diammonium phosphates, ammonium sulfate and dicalcium phosphate. The latter component is exclusively in citrate-soluble form. A process flow diagram was developed and the material balance of enriched superphosphate and ammophosphate in a single process cycle was calculated. The some superior parameters of ammophosphate are: good commodity properties (granularity, granule hardness), good water solubility and content other nutrient components (sulfur and calcium).

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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