Improved diammonium phosphate from Tahoua natural phosphate and synthetic diammonium phosphate

Abstract

Phosphate is an essential nutrient for plants and is used in the formation of diammonium phosphate (DAP) fertilizer. Natural phosphate of Tahoua being low grade, has a range of impurities and cannot be used by the conventional method to prepare good quality DAP. However, this rock can be used by some unconventional techniques to prepare better quality fertilizer to meet the nutrient requirements of plants. This study aims to prepare a good quality improved diammonium phosphate fertilizer in order to evaluate its phosphorus availability in the perchloric acid solution and in distilled water. The commercial phosphate powder is mixed with synthesized diammonium phosphate fertilizers. The reaction mixture was carried out at an NH_3:H_3PO_4 molar ratio of 2. The fertilizer obtained was characterized with X-ray diffraction and infrared spectrophotometry. These analyzes showed no change in structural properties. But, we see a change in nutritional properties which corresponds to the increase in the phosphate content which will be available to the plants. Thus, the forms of P fertilizer studied will make it possible to improve productivity, sustainable use of resources and a reduction in production costs for these crop systems.

Key words: diammonium phosphate, natural phosphate, dissolution, perchloric acid, water

I. Introduction

In Niger, cultivated soils are often deficient in fertilizing elements (phosphorus, nitrogen). They deserve a contribution to improve the quality of the soil in terms of fertilizing elements. However, these fertilizing elements play an important role in the vegetative cycle of plants and promote increased agricultural yields [1]. They are also used to manufacture binary fertilizer (NP) commonly called diammonium phosphate (DAP) [2, 3]. It is a crystalline product completely soluble in water, is used as a raw material for the preparation of water-soluble NPK fertilizers for protected and open soils [3]. Diammonium phosphate fertilizer is manufactured by the reaction which takes place between phosphoric acid and ammonia, and is mainly used as a base fertilizer for sowing on soils rich in potash or as a supplement to potash fertilizer. It provides easily soluble nutrients (phosphorus and nitrogen) at the start of crops. When applied in the food of the plant species it increases the pH of the soil in some time, unfortunately in the long run the soil becomes more acidic than before during ammonium nitrification. DAP phosphate, perfectly soluble in water, helps meet the needs of the plant. Then it is also used as a starter fertilizer and presents a phosphate ion in the form of the divalent ion $H_2PO_4^{2-}$. It must find H^+ ions in a soil solution for it to become monovalent HPO_4^-. This is very difficult on limestone soil [4]. Indeed, the DAP prepared contains trace elements, especially since the phosphoric acid used is raw, unpurified. The elements can be heavy metals and transfer to fertilizers and then into crops [5]. However, this fertilizer is recommended to be applied in spring, which provides the crop with available phosphorus at the same time as nitrogen.

II. Materials and methods

II.1. Improvement of the P_2O_5 content of DAP

II.1.1. Reagents and solutions

The chemicals used for the preparation of improved diammonium phosphate are prepared from NORMAPUR brand commercial solutions:

- ✓ phosphoric acid (H_3PO_4) is 98% by mass and its density is 1.88;
- ✓ ammonia (NH3) is 85% by mass and density 0.73;

The solutions used for the dissolution of improved diammonium phosphate are prepared from commercial NORMAPUR brand solutions:

- ✓ perchloric acid ($HClO_4$) is 65% by mass and its density is 1.61;
- ✓ distilled water

II.1.2. Sample particle sizes

Natural phosphate of Tahoua has been crushed and ground to obtain the targeted quality. It is a nodular type sedimentary phosphate and has a total content of around 30% on average. Then, three meshes (63; 100 and 160 µm) of powder of this phosphate were used. The powder of phosphate merchant of Tahoua is shown in Figure II.1.

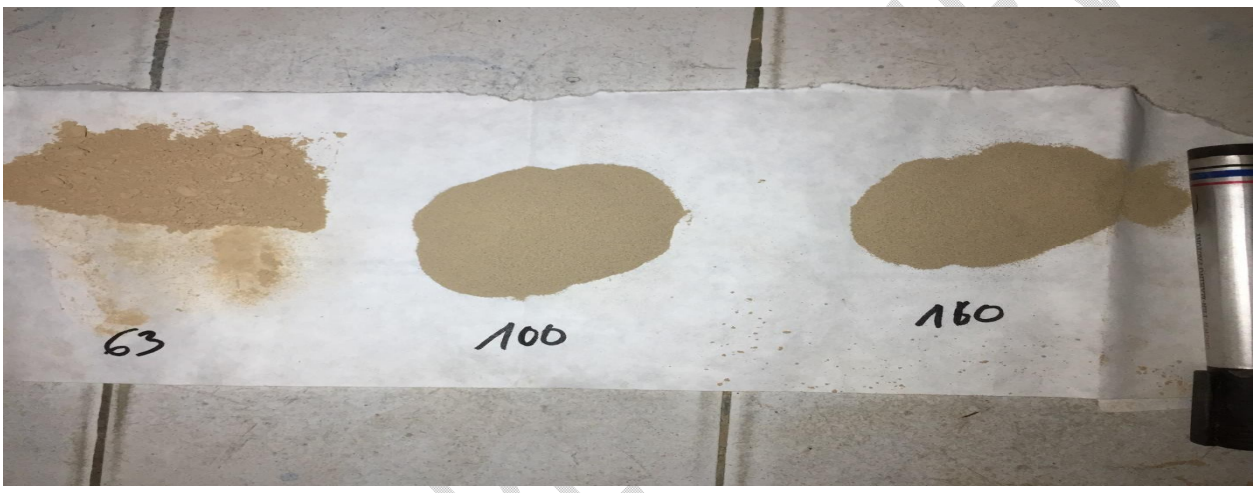

Figure. 1: Photograph of merchant phosphate in grain sizes 63; 100; 160 µm

II.1.3. Synthesis of diammonium phosphate

All reagents used were of analytical quality. Diammonium phosphate is a simple salt, but a complex fertilizer, as it is a source of the two nutrients nitrogen and phosphorus. It can be made by partially neutralizing dilute phosphoric acid with a dilute ammonia solution. Ammonia is titrated with phosphoric acid to form diammonium hydrogen phosphate, see the following reaction:

$$H_3PO_4 + 2NH_3 \rightarrow (NH_4)_2HPO_4$$

The neutralization reaction of phosphoric acid by gaseous ammonia is an exothermic reaction. The experiment was carried out at pH equal to 8 and at ambient laboratory temperature. The products obtained were then dried in an oven at 60°C and stored in a desiccator. The phosphate merchantTahoua samples were then spiked with the product obtained in different quantities to determine the dissolved P2O5 content (Table I).

Table I: Samples prepared

Particle sizes	PNTs (%)	DAP (%)

63 µm	95	5
	90	10
	85	15
	80	20
100 µm	95	5
	90	10
	85	15
	80	20
160 µm	95	5
	90	10
	85	15
	80	20

II.1.4. Analysis of the products obtained

Improved diammonium phosphate fertilizer was analyzed by X-ray fluorescence and infrared spectrometry.

III. Results and discussion

III.1. synthesis of DAP and improvement of dissolved P_2O_5 content

III.1.1. Synthesis of diammonium phosphate

As a first step, we began the synthesis of a diammonium phosphate fertilizer by neutralizing phosphoric acid with ammonia (final pH 7.95). The precipitate obtained is shown in figure III.2:

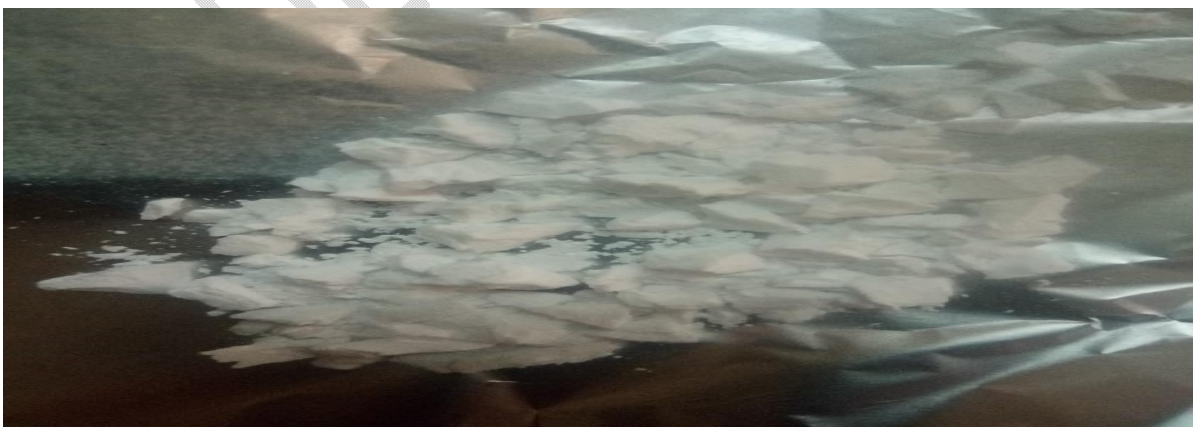

Figure.2: Photograph of diammonium phosphate precipitate

The photograph in this figure shows the diammonium phosphate precipitate. And the precipitate has been well crystallized. It constitutes two essential nutrients whose structure should consist of less than 30% nitrogen (N) and more than 70% phosphorus (P). It should not be exposed to the open air, as it will gradually lose ammonia. This fertilizer is popular because of its relatively high nutrient content and excellent physical properties. Previous studies have shown a standard quality of 46% phosphate and 18% nitrogen [6, 7]. The elements nitrogen and phosphorus found in it, in the form of ammonium (NH_4) and phosphate (P_2O_5), have a particularly positive effect during the first period of plant development. As a result, DAP is a highly soluble by-product, dissolving rapidly in the soil to release the phosphate and ammonium available to plants.

III.1.2. Dissolution of improved diammonium phosphate (DAPA)

A mixture of Tahoua market phosphate and diammonium phosphate was used to increase the phosphorus content. The rock phosphate used is a sedimentary phosphate made up mainly of fluorapatite, with an average content of around 30% P_2O_5, but it does contain impurities [8]. The decomposition reaction of fluoroapatite takes place on the surface of solid materials without a catalyst. So, dissolution of solid materials takes place by breaking the lowest-energy bonds. On the other hand, P-O bonds are not broken so that the structure is not completely destroyed [9]. In an acidic environment, phosphate in the form of PO_4^{3-} ions captures H+ ions to form HPO_4^{2-} or $H_2PO_4^-$ ions, depending on the strength of the acid. This is the decomposition reaction between fluoroapatite [10] and diammonium phosphate fertilizer decomposed in solution. The balance equation for the dissolution reaction is shown below:

$$Ca_{10}(PO_4)_6F_2 + (NH_4)_2HPO_4 + 15H^+ \rightarrow 10Ca^{2+} + 7H_2PO_4^- + 2HF + 2NH_4^+$$

As shown in the equation, the dissolution of the improved DAP fertilizer results in the consumption of proton H^+, the release of ammonium ions NH_4^+ and the formation of hydrofluoric acid. We then studied the dissolution of ores in perchloric acid and distilled water. This was carried out with the aim of assessing the level of dissolved P_2O_5 by measuring P_2O_5 in the various filtrates collected after etching. The results of this study will be presented and discussed in the following paragraphs.

III.1.2.1. Solubility of DAPA in distilled water

We dissolved diammonium phosphate fertilizer in water. The results obtained are shown in figure III.3. She represents the dissolution rate of improved DAP in water.

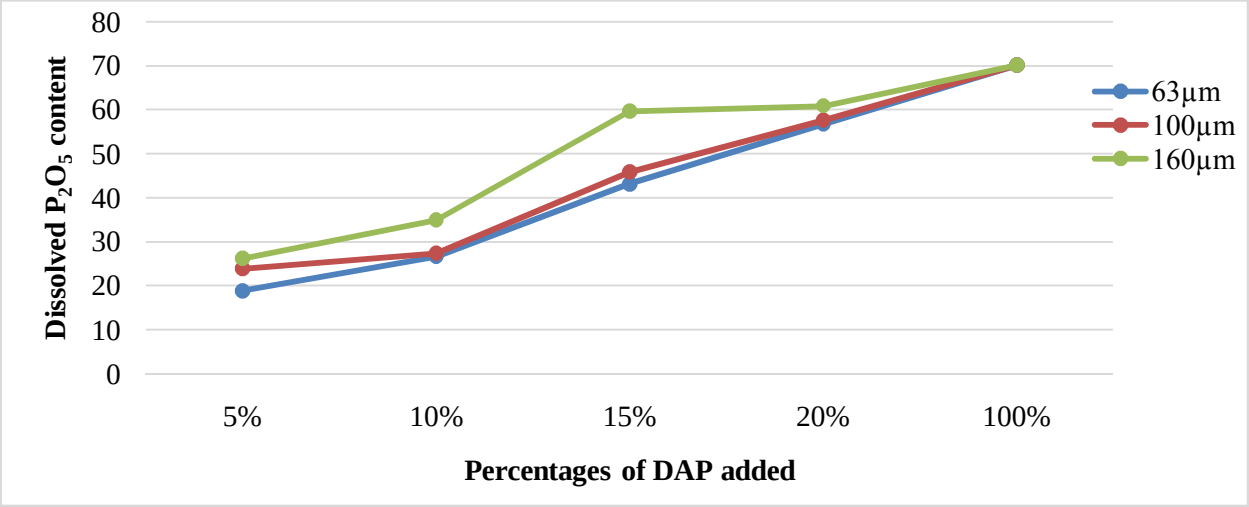

Figure. 3: Dissolved P_2O_5 content of DAPA in water

Analyses of the dissolution of improved diammonium phosphate (DAPA) in distilled water clearly show that P_2O_5 rates increase when the amount of DAP is increased. The best dissolution rates of improved diammonium phosphate fertilizer are obtained when 20% DAP is added to 160 µm rock phosphate, and the lowest rate of DAPA dissolution in distilled water is obtained when 5% DAP is added. This shows that the combination of Tahoua rock phosphate with diammonium phosphate fertilizer resulted in an increase in water-soluble P_2O_5. Any small amount of DAP added to rock phosphate significantly improves the rate of phosphate dissolution in solution. This sharp rise in the rate of DAPA dissolution could be attributed to the addition of DAP to TNP, which is overloaded with metallic elements, influences its solubility, and is perfectly soluble in water. Similar results have been observed on the dissolution of diammonium phosphate fertilizers with the addition of the products [11, 12]. Although we haven't yet applied it in agriculture, the results obtained could increase the agronomic efficiency of the crop. In fact, it provides a rapid response to the plant's needs during start-up, as it acts directly on the roots to enhance plant development. In this case, the phosphate ion is presented in the form of the bivalent HPO_4^{2-} ion, and to become monovalent $H_2PO_4^-$, it must find an H^+ proton in the medium. The increase in solubility can be explained by the release of phosphate particles from the decomposition of DAP in this medium. This results in a significant consumption of H^+ ions in the medium, increasing the dissolution of ores [13, 14]. The products obtained must therefore be of high solubility, less expensive and give good yields in agricultural production, especially if used at the time of sowing with grain as a starter fertilizer. Because of its nitrogen content, it is imperative for crops that need these nutrients in their initial phase. Nitrogen doesn't change its structure, so it can be used by plants. However, there are several ways in which rock phosphate can be improved to enhance its solubility. So, it is noted that this improved diammonium phosphate fertilizer is a beneficial product for farmers.

III.1.2.2. Solubility of DAPA in perchloric acid solution

Determination of phosphoric anhydride in filtrates from the attack of improved diammonium phosphate with NTP:DAP ratios of 95:5; 90:10; 85:15 and 80:20 by perchloric acid solution gave the results shown in figure 25. The results obtained after dissolution of DAPA are respectively at 5% (50.55%; 43.85%; 45.33%); 10% (48.90%; 46.88%; 43.70%); 15% (52.70%; 54.9%; 54.83%); 20% (60.67%; 63.95%; 60.44%). Next, the results of the dissolution of the synthesized DAP obtained are respectively 76% total phosphate and 70.12% water-soluble phosphate (i.e. 30.62% phosphorus). We note an increase in dissolved P_2O_5 content regardless of the small portion of DAP fertilizer added to the NTP. The P_2O_5 content is higher in the 63 micrometer NWP particle size range with the addition of 5-10% DAP, whereas with the addition of 15-20% DAP, it is higher for particle sizes greater than or equal to 100 micrometers. This increase in dissolution rate could be linked to the specific surface area of the phosphate particles and the addition of DAP. DAP is completely dissolved in the acid solution. In this case, several studies have been carried out on the evolution of phosphoric anhydride content as a function of percentage and particle size. The results found are identical to those observed in the case of phosphate attack by conventional acid solutions, but the dissolution of solutions of this acid is much greater [6, 12]. The results of this study show that the extent of dissolution depends on the addition of DAP, particle sizes and the attack of hydronium ions H_3O^+. Overall, we found significant consumption of H_3O^+ ions in the medium. This phenomenon could be explained by the strength of the acidity of this acid [13]. These results are comparable to those found by several studies such as: Von Semel and colleagues manufactured the fertilizer to obtain good quality crystalline ammonium phosphate using ammonia and technical grade phosphoric acid, which was freed of most of the impurities after precipitation in an organic solvent [16]. The DAPA solubilization rates we obtained are higher than those obtained by [14, 16] for the dissolution of merchant phosphate from Tahoua; calcined rock phosphate from Tahoua [13].

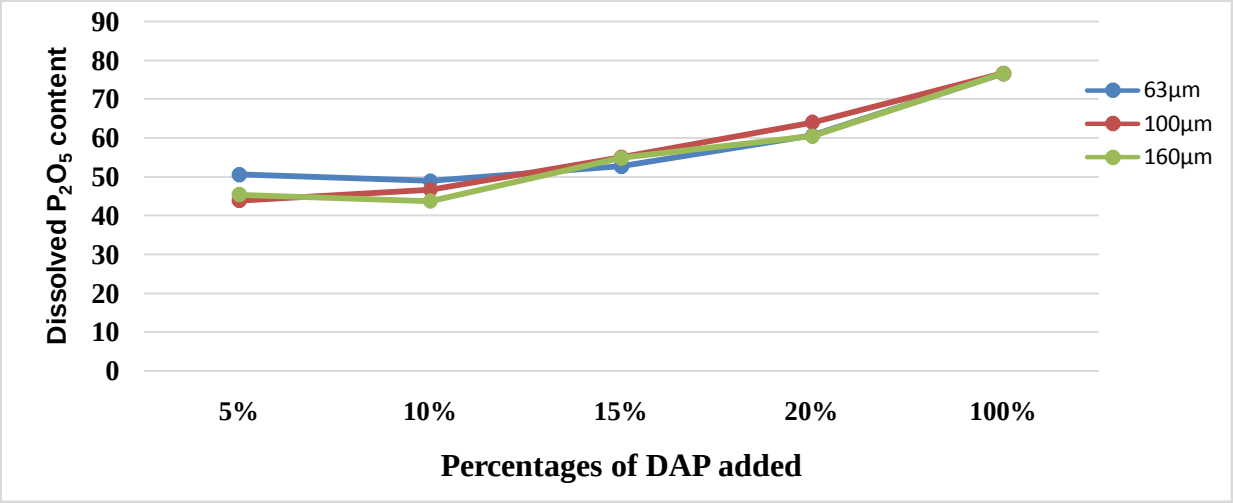

Figure.4: Dissolved P_2O_5 content of DAPA in perchloric acid

III.1.2.3. X-ray diffraction

X-ray diffraction analysis shows that the product obtained from the neutralization reaction of Tahoua rock phosphate and synthetic diammonium phosphate contains no lines other than those of the improved diammonium phosphate. However, it cannot be ruled out that the initial powders contain other phases in quantities small enough to be detected by X-rays. But also, other amorphous impurities. The results of these analyses are shown in figure III.5:

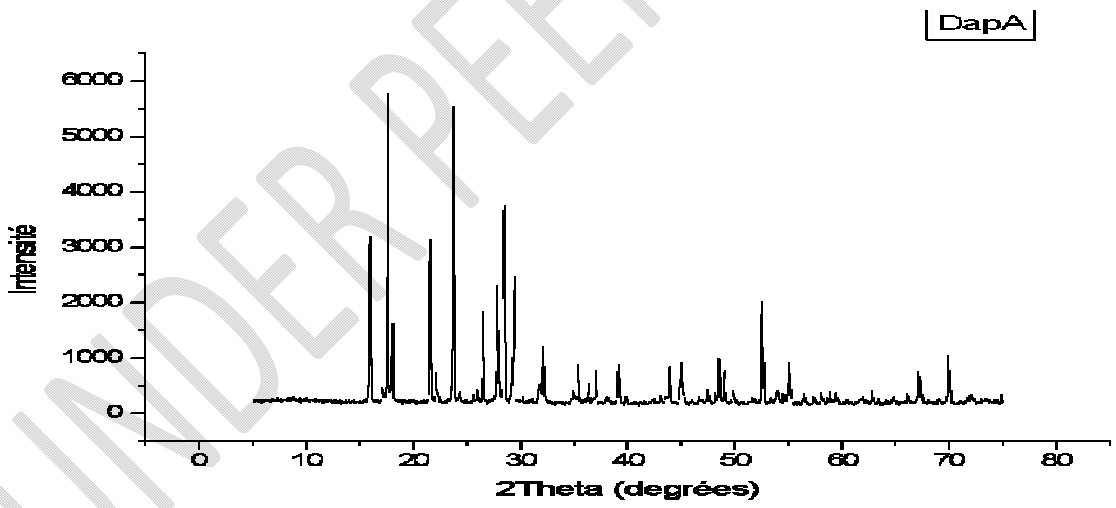

Figure.5:Diffractogram X-ray of diammonium phosphate

III.1.2.4. Infrared spectrometry

Infrared spectrometric analysis (Figure III.6) of the product obtained identifies several bands, in particular those attributable to phosphate ions and water molecules. We attribute the bands around 3175,2966, 2743,2206 2124, 1923,1714, 1446 and 1400 cm-1 to the vibrations of ammonium ions NH_4^+ and these lines are attributed to the vibrations of phosphate ions 894, 939, 1043 and 1192 in the infrared spectrum of diammonium phosphate fertilizer.

Table II: Band IR positions and intensities.

	Position des bandes (cm^{-1})	Intensités
1	894.56108	39.34475
2	939.28913	35.46498
3	1043.65459	42.79041
4	1192.74811	75.19830
5	1446.20708	48.94742
6	1714.57541	76.84278
7	1923.30632	73.74736
8	2124.58257	78.71972
9	2206.58400	75.35291
10	2743.32065	51.25275
11	2966,9609	65,10515
12	3175,6918	78,94623

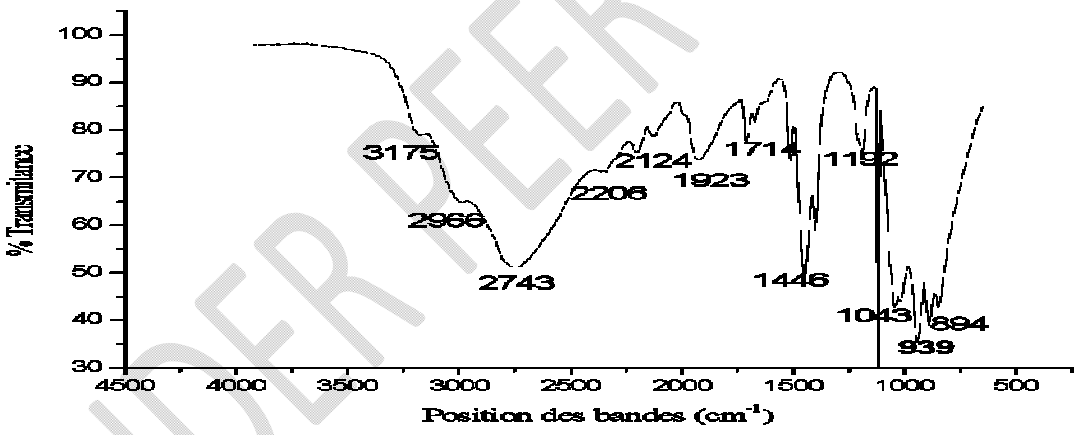

Figure.6: Infrared spectrum of diammonium phosphate

Conclusion

The pH of the reaction mixture represents a control parameter that enables the process of neutralizing phosphoric acid with ammonia to be properly managed. The addition of the product obtained in the various Tahoua rock phosphate fractions yields a significant diammonium phosphate pro-product. Chemical analysis of the products obtained showed that the addition of diammonium phosphate up to a content of 20% in rock phosphate significantly enhances the nutritional properties of the fertilizers in terms of phosphorus content. X-ray diffraction analysis shows that there are no structural changes in the products obtained in relation to the increase in phosphate content. Similarly, infrared spectra did not confirm the formation of new chemical compounds with the phosphates present in the system.

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