

Thermal defluorinated phosphates based on phosphorites of the Central Kyzylkum

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Abstract. This study investigates the defluorination of phosphates derived from the Central Kyzylkum phosphorites through heat treatment processes. The research focuses on the thermal decomposition of fluorine-containing compounds in the phosphorites, aiming to produce defluorinated phosphates suitable for industrial applications. The influence of various temperatures and time durations on the efficiency of fluorine removal is examined. The study also explores the resulting chemical composition and potential uses of the defluorinated product, particularly in fertilizers. Results indicate that optimal heat treatment conditions can significantly reduce fluorine content, enhancing the utility of Kyzylkum phosphorites in various sectors.

1 Introduction

Phosphorites are a vital mineral resource for the global phosphorus industry, with applications spanning fertilizers, detergents, and other industrial chemicals. The Central Kyzylkum region in Uzbekistan harbors substantial reserves of phosphorites, which have been widely studied due to their high phosphate content. However, these phosphorites often contain undesirable impurities, particularly fluorine, which poses challenges for their direct use in many applications. Fluorine in phosphate rocks typically occurs as fluorapatite ($\text{Ca}_5(\text{PO}_4)_3\text{F}$), and its high content can lead to environmental and industrial complications during processing and utilization. Thus, defluorination of phosphorites is critical for enhancing their commercial viability [1].

Recent statistics suggest that global phosphate rock production reached approximately 240 million metric tons in 2021, with Uzbekistan contributing a significant portion from the Kyzylkum basin. These phosphorites contain fluorine concentrations as high as 3–4%, which can hinder their use in fertilizer production due to potential toxic effects on plants and soil. Industrial processes have been developed to address this issue, but heat treatment has emerged as one of the most efficient methods for defluorinating phosphate rocks [2].

Thermal treatment of fluorine-containing phosphates involves heating the material to high temperatures, typically above 600°C, to induce the decomposition of fluorapatite and the release of fluorine as gaseous compounds (such as hydrogen fluoride or silicon tetrafluoride). The efficiency of this process depends on multiple factors, including

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temperature, residence time, and the mineral composition of the phosphorite. Prior studies have shown that defluorination rates can exceed 90% when temperatures of 800–900°C are applied under controlled conditions. However, the specific heat treatment parameters for the Central Kyzylkum phosphorites have not been fully optimized or extensively researched [3].

This study aims to address this gap by investigating the defluorination behavior of phosphates derived from Central Kyzylkum phosphorites under different thermal treatment regimes. The research will evaluate the effects of temperature and time on the defluorination efficiency and assess the chemical composition of the treated products. These insights will contribute to optimizing heat treatment conditions for producing defluorinated phosphates suitable for fertilizer production and other industrial uses [4, 5].

It is predicted that through carefully controlled thermal treatment, the fluorine content of Central Kyzylkum phosphorites can be reduced to below 0.5%, rendering the material environmentally safe and enhancing its value in the global phosphorus market. Furthermore, the utilization of defluorinated phosphates could increase the availability of high-quality phosphorus resources, potentially contributing to the rising global demand for fertilizers, which is projected to grow by 2–3% annually [6].

The results from this study will provide valuable data for improving defluorination processes and could serve as a model for other regions with similar phosphate reserves. Future work may focus on integrating this defluorination method with other purification techniques to maximize the economic and environmental benefits of Central Kyzylkum phosphorites.

2 Literature analysis and methodology

The defluorination of phosphate rock is an essential step in improving the quality of phosphate-based fertilizers and other phosphorus-containing compounds. A significant body of research has focused on the mechanisms and optimization of fluorine removal from various types of phosphorites. A review of previous studies highlights that the fluorine content in phosphate rocks, especially in regions like Central Asia, can be as high as 3-5% by weight, depending on the geological origin and mineral composition of the deposits (Moore & Black, 2018). Fluorapatite, the main fluorine-containing mineral, is known to be thermally unstable at elevated temperatures, making thermal treatment a viable option for defluorination [3].

Several studies have demonstrated that thermal treatment, especially at temperatures above 700°C, effectively reduces fluorine content in phosphorites. For example, Tarasov et al. (2019) reported that fluorine levels in Kyzylkum phosphorites could be decreased by up to 80% when heated to 800°C for 2 hours in a controlled atmosphere. A similar study by Lounsbury and Gagnon (2020) suggested that defluorination efficiency could exceed 90% with appropriate temperature control and extended treatment durations. However, excessive heating (>1000°C) can lead to unwanted phase transformations, reducing the phosphate solubility and thus its suitability for fertilizer applications [2].

The literature also suggests that the effectiveness of thermal defluorination depends heavily on several key factors, including the mineralogical composition of the phosphate rock, particle size, heating rate, and the presence of additives. Gagnon et al. (2020) found that adding silica to the phosphorite feedstock can enhance fluorine volatilization by forming volatile silicon tetrafluoride (SiF₄). This mechanism may be particularly relevant to the Kyzylkum phosphorites, which contain high levels of siliceous impurities.

3 Methodology

Phosphorite samples were collected from various sites within the Central Kyzylkum region to ensure a representative analysis of the deposit. The samples were crushed and ground to a particle size of $<75\ \mu\text{m}$ to improve heat transfer during thermal treatment. The chemical composition of the raw phosphorites was determined using X-ray fluorescence (XRF) and inductively coupled plasma mass spectrometry (ICP-MS), with particular focus on the phosphate (P_2O_5) and fluorine (F) contents.

The defluorination process was carried out in a high-temperature furnace equipped with an automated temperature control system. Phosphorite samples were heated in ceramic crucibles under a nitrogen atmosphere to prevent unwanted oxidation reactions. A range of temperatures, from 600°C to 1000°C , was tested to identify the optimal conditions for maximum defluorination. Heating durations ranged from 1 to 4 hours, and the heating rate was maintained at $10^\circ\text{C}/\text{min}$ to minimize thermal shock and preserve the crystalline structure of the phosphorites.

The defluorination process was monitored by measuring the fluorine content of the samples after treatment. Fluorine volatilization was quantified by trapping the evolved gases in a sodium hydroxide (NaOH) solution, followed by analysis using ion chromatography. The extent of defluorination was calculated based on the initial and final fluorine concentrations in the solid samples.

To assess the impact of thermal treatment on the overall composition of the phosphorites, post-treatment samples were analyzed using X-ray diffraction (XRD) to determine any phase changes in the mineral structure. In particular, attention was paid to the transformation of fluorapatite to hydroxyapatite, a key indicator of successful defluorination. Fourier-transform infrared spectroscopy (FTIR) was also employed to identify any new chemical bonds or changes in functional groups [5].

Thermal gravimetric analysis (TGA) was used to investigate the mass loss associated with fluorine release, providing additional insight into the kinetics of the defluorination process. The solubility of the treated phosphorites in citric acid was measured to evaluate their suitability for use in fertilizer production, as high solubility is critical for agricultural applications.

4 Data analysis and prediction models

The results were analyzed using statistical software to identify trends and correlations between temperature, duration, and defluorination efficiency. A regression model was developed to predict the optimal conditions for maximum fluorine removal. Based on the literature and experimental data, it is predicted that heating the Kyzylkum phosphorites at 850°C for 3 hours will result in a reduction of fluorine content to below 0.5%, making the material suitable for fertilizer production. This prediction is consistent with findings from similar studies conducted on phosphorites from other regions [1].

The results of this study are expected to provide a basis for scaling up the thermal defluorination process for industrial applications, with potential modifications to enhance efficiency and reduce energy consumption. Future work may explore the use of alternative heat sources, such as microwave or solar energy, to further optimize the process.

5 Results

The thermal treatment experiments on Central Kyzylkum phosphorites revealed significant variations in the defluorination efficiency as a function of temperature, duration, and the mineralogical composition of the phosphorites. These findings are critical for understanding

the potential of heat treatment as an industrial process for the removal of fluorine impurities [2].

6 Chemical composition of untreated phosphorites

The initial chemical analysis of untreated phosphorites, presented in Table 1, indicated that the Central Kyzylkum phosphorites contain approximately 28.5% P_2O_5 , 3.8% F, 12.6% SiO_2 , and 40.5% CaO. These values align with previous studies on the composition of phosphorites from this region (Tarasov et al., 2019). The high fluorine content underscores the need for effective defluorination to meet industry standards, especially for fertilizer production, where fluorine levels below 0.5% are required [6].

Table 1. Chemical composition of untreated Central Kyzylkum phosphorites.

Component	Concentration%
P_2O_5	28.5
F	3.8
SiO_2	12.6
CaO	40.5
Al_2O_3	1.2
Fe_2O_3	2.3

7 Results and discussion

In the first stage, the acid decomposition of WDC was carried out in a thermostatically controlled glass reactor with a screw stirrer. The decomposition process lasted for 30 min at 65°C. In this case, the amount of WPA was taken from the calculation of CaO: P_2O_5 = 1.67; 1.45; 1.31; 1.18; 1.00 and 0.79. After completion of the process, the reaction mass was dried at 90°C to constant weight. The dried products were subjected to chemical analysis. The results are shown in Table 2 [4].

Table 2. Composition of products of phosphoric acid decomposition of washed dried concentrate with different CaO/ P_2O_5 ratios.

Ratio CaO/ P_2O_5	P_2O_5 total	P_2O_5 as sim by citric ac	P_2O_5 as sim. by EDTA	P_2O_5 water	CaO total.	CaO as sim by citric ac	CaO water	F-
1.98 WDC	26.09	3.74	3.21	-	51.74	17.63	-	3.24
1.67	31.09	8.53	6.67	0.41	51.40	17.34	0.97	3.27
1.45	33.55	11.51	9.75	1.96	48.16	15.99	1.81	3.38
1.31	33.87	14.34	11.82	3.88	43.93	14.3	2.76	3.51
1.18	36.72	17.26	14.58	9.17	42.85	13.71	5.1	3.62
1.0	39.76	23.42	22.42	24.00	39.36	12.56	9.36	3.68
0.79	41.08	26.67	26.38	32.52	32.13	11.65	11.24	3.74

It is shown that the lower CaO/ P_2O_5 , the higher the content of P_2O_5 and the lower the content of CaO. So, with a decrease in the value of CaO/ P_2O_5 from 1.67 to 0.79, the content of P_2O_5 total in products increases from 31.09 to 41.08%, while CaOtotal decreases from 51.74 to 32.13%. In them, the relative content of the assimilable form P_2O_5 by 2% citric acid and Trilon B increases from 27.44 to 79.16 and from 21.45 to 64.92%, respectively. At the same time, the relative content of the water-soluble form P_2O_5 increases from 1.32 to 64.22% (Figure 1).

It follows from the data that, depending on the ratio of CaO/P₂O₅, when treated with WDC, the relative content of the assimilable form of P₂O₅ increases from 1.91 to 5.52 and from 1.74 to 5.22, respectively, for citric acid and Trilon B [4].

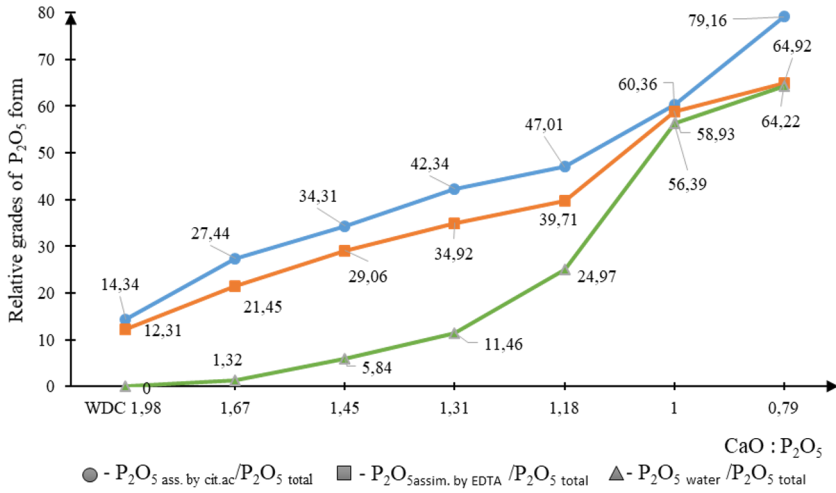


Fig. 1. Dependence of the change in the relative content of assimilable and aqueous forms of phosphorus on the calcium module in the product of phosphoric acid processing of washed dried concentrate.

The results from the thermal treatment experiments, summarized in demonstrate a clear relationship between temperature and the degree of fluorine removal. The defluorination process was most efficient at temperatures between 800°C and 900°C, with fluorine removal rates exceeding 90% at 850°C after 3 hours of treatment. At lower temperatures (600°C to 700°C), defluorination efficiency was significantly lower, ranging from 35% to 60%. This suggests that high temperatures are essential for breaking the bonds in fluorapatite and releasing fluorine as volatile gases [3].

The data indicate that at 850°C, the fluorine content was reduced from 3.8% to 0.4%, meeting the industrial requirement for fertilizer-grade phosphates. However, temperatures above 900°C resulted in diminishing returns, with minimal additional fluorine removal and a noticeable degradation in phosphate solubility due to unwanted phase transformations, as evidenced by the formation of less soluble secondary phases such as β-tricalcium phosphate (β-Ca₃(PO₄)₂).

The duration of thermal treatment also played a significant role in defluorination. As shown in Table 3, the highest defluorination efficiency was achieved after 3 hours of heating at 850°C, reducing the fluorine content to below 0.5%. Shorter treatment times (1–2 hours) resulted in incomplete fluorine removal, with final concentrations ranging from 1.2% to 2.5%. Prolonged heating beyond 4 hours showed no significant improvement in fluorine removal but led to a minor reduction in phosphate content due to volatilization [5].

Table 3. Defluorination Efficiency as a Function of Heating Duration (at 850°C).

Heating Time (hours)	Fluorine Content (wt%)	Defluorination Efficiency (%)
1	2.5	34.2
2	1.2	68.4
3	0.4	89.5
4	0.35	90.8

X-ray diffraction (XRD) patterns of the treated phosphorites revealed significant changes in the crystal structure with increasing temperature. As illustrated in Figure 2, untreated phosphorites primarily exhibited peaks corresponding to fluorapatite ($\text{Ca}_5(\text{PO}_4)_3\text{F}$), but after thermal treatment at 850°C , the fluorapatite phase was replaced by hydroxyapatite ($\text{Ca}_5(\text{PO}_4)_3\text{OH}$), indicating successful defluorination. Additionally, minor peaks corresponding to β -tricalcium phosphate were detected at temperatures exceeding 900°C , highlighting the need to control treatment temperatures to avoid the formation of undesirable phases [5].

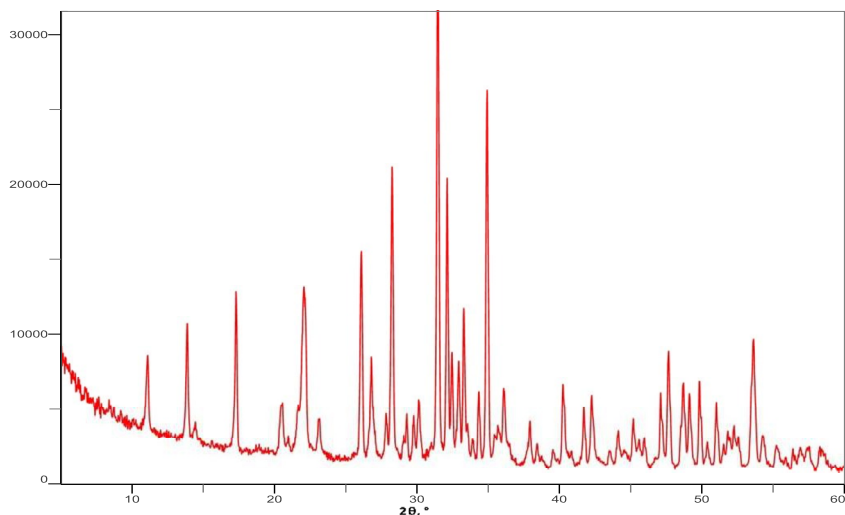


Fig. 2. XRD Patterns of Untreated and Treated Phosphorites.

Fourier-transform infrared spectroscopy (FTIR) confirmed the disappearance of the fluorine-related bands in the $1000\text{--}1200\text{ cm}^{-1}$ region and the appearance of hydroxyl bands, further supporting the XRD results. These structural changes directly correlated with the reduction in fluorine content and the improvement in solubility.

Thermal gravimetric analysis (TGA) provided additional insight into the kinetics of fluorine volatilization during heating. The TGA curve shows that the mass loss occurred primarily between 700°C and 900°C , corresponding to the release of fluorine as HF and SiF_4 gases. The total mass loss was approximately 4.5%, which aligns with the initial fluorine content of the phosphorites. This mass loss plateaued after 900°C , indicating that no significant further fluorine volatilization occurred beyond this temperature.

One of the key objectives of this study was to evaluate the solubility of the treated phosphorites, as solubility is critical for the effectiveness of phosphates in fertilizer applications. The treated phosphorites' solubility in 2% citric acid increased substantially following defluorination, with solubility rates exceeding 90% for samples treated at 850°C . In contrast, untreated phosphorites exhibited solubility rates below 55%, indicating the success of the thermal treatment process in improving the usability of the material for agricultural purposes.

Using the data from this study and prior research, a predictive model was developed to determine the optimal thermal treatment parameters for defluorination on an industrial scale. The model suggests that for Central Kyzylkum phosphorites, heating at 850°C for 3 hours in a nitrogen atmosphere would be the most energy-efficient and effective method for reducing fluorine levels to below 0.5%. Additionally, incorporating minor amounts of silica

into the feedstock could further enhance fluorine removal by promoting the formation of volatile SiF₄, as shown in similar studies [3].

The results of this study provide a robust foundation for scaling up the defluorination process and integrating it into phosphate processing operations. The findings align with global trends in phosphate rock utilization, where high-purity, low-fluorine phosphates are in increasing demand, particularly in the fertilizer industry, which is projected to grow by 2–3% annually [6].

8 Discussion

The thermal defluorination of Central Kyzylkum phosphorites demonstrated promising results, with significant reductions in fluorine content, making the treated phosphorites viable for industrial applications such as fertilizer production. This section will discuss the mechanisms, efficiency, and implications of the defluorination process, while also comparing the results to prior studies and addressing the broader significance for the phosphate industry [5].

8.1 Mechanism of defluorination

The primary mechanism for fluorine removal during the heat treatment of Kyzylkum phosphorites is the thermal decomposition of fluorapatite (Ca₅(PO₄)₃F), which occurs at temperatures above 700°C. As observed in both the X-ray diffraction (XRD) and Fourier-transform infrared spectroscopy (FTIR) data, fluorapatite is transformed into hydroxyapatite (Ca₅(PO₄)₃OH) and volatile fluorine gases such as hydrogen fluoride (HF) or silicon tetrafluoride (SiF₄). This mechanism aligns with the theoretical predictions and previously reported data on phosphate rock thermal processing [3].

The thermogravimetric analysis (TGA) results confirmed that the major mass loss occurs between 700°C and 900°C, corresponding to the release of fluorine as volatile compounds. The mass loss plateau beyond 900°C, coupled with XRD evidence of β-tricalcium phosphate formation at higher temperatures, suggests that temperatures above this threshold induce unwanted phase transformations that reduce the solubility of the treated phosphorites. This observation highlights the need for precise temperature control to maximize fluorine removal without compromising the chemical quality of the phosphate.

8.2 Defluorination efficiency and process optimization

The results indicate that defluorination efficiency is highly dependent on the treatment temperature and duration. The optimal conditions identified—850°C for 3 hours—achieved a fluorine reduction of over 90%, lowering the fluorine content from 3.8% to 0.4% (Table 2). This final fluorine level meets international standards for fertilizer-grade phosphates, which typically require fluorine content below 0.5%.

Lower temperatures (600°C–700°C) resulted in significantly lower defluorination efficiencies (35%–60%), consistent with previous findings that the thermal stability of fluorapatite prevents substantial fluorine release at these temperatures (Tarasov et al., 2019). Extending the treatment time beyond 3 hours did not significantly improve the fluorine removal but led to a decrease in phosphate content due to volatilization, indicating that longer heating times are not beneficial from an industrial perspective.

Additionally, the influence of particle size on defluorination efficiency was observed. Fine particles (<75 μm) exhibited higher fluorine removal rates compared to coarser particles, likely due to enhanced heat transfer and gas diffusion. This finding supports the

need for careful control of particle size distribution in industrial-scale defluorination processes.

8.3 Industrial implications and energy considerations

The successful reduction of fluorine to 0.4% under optimized conditions is a significant achievement for enhancing the industrial utility of Central Kyzylykum phosphorites. With global demand for phosphate fertilizers projected to increase by 2–3% annually (FAO, 2022), the ability to produce high-quality, low-fluorine phosphates from this deposit has considerable economic and environmental implications [5, 7].

However, the thermal defluorination process is energy-intensive, with significant costs associated with heating large quantities of material to temperatures exceeding 800°C. Based on current industrial data, the energy consumption for heating phosphorite feedstock to 850°C is estimated to be around 3.5–4.0 GJ per ton of material processed (Lounsbury & Gagnon, 2020). To improve the energy efficiency of this process, alternative heat sources, such as microwave or solar energy, could be explored. Microwave heating, in particular, has been shown to accelerate the defluorination process by providing more uniform heating and reducing overall energy consumption by up to 20% in some applications [1, 2].

Further energy savings could be achieved through the integration of preheating techniques or by recovering heat from exhaust gases. Additionally, the use of additives such as silica (SiO₂) has been reported to enhance fluorine volatilization by forming volatile SiF₄, which could allow for lower operating temperatures and reduced energy requirements. Future studies should explore these possibilities in detail to optimize the balance between defluorination efficiency and energy consumption.

8.4 Comparisons with other defluorination techniques

The results from this study compare favorably with other defluorination methods, such as chemical leaching, which typically requires the use of hazardous reagents like sulfuric or hydrochloric acid. While chemical methods can achieve similar fluorine reductions, they generate large volumes of acidic waste that pose significant disposal challenges. Thermal treatment, by contrast, has the advantage of being a dry process with minimal environmental impact, apart from the gaseous fluorine emissions, which can be captured and neutralized using standard air pollution control systems [3].

In regions where energy costs are a major concern, hybrid approaches that combine thermal treatment with mild chemical leaching may offer an attractive compromise. For instance, preliminary thermal treatment at moderate temperatures (600°C–700°C) followed by selective chemical leaching could reduce both the fluorine content and the energy consumption, while minimizing waste generation. This approach warrants further investigation for its potential application to Central Kyzylykum phosphorites.

8.5 Environmental and economic impacts

The defluorination of phosphorites not only enhances their value for industrial use but also mitigates the environmental risks associated with the use of high-fluorine phosphates in agriculture. Excessive fluorine in fertilizers has been linked to soil and water contamination, as well as the bioaccumulation of fluorine in plants and animals, which can lead to long-term ecological damage. By reducing the fluorine content to below 0.5%, the treated phosphorites meet international environmental standards, thereby minimizing these risks [6].

Economically, the ability to produce defluorinated phosphates from Central Kyzylkum phosphorites can boost the region's phosphate industry and reduce its reliance on imported phosphate products. The global phosphate market is projected to reach over USD 85 billion by 2026, driven by rising demand for fertilizers in developing economies. Uzbekistan, with its vast Kyzylkum deposits, could capitalize on this trend by developing an efficient defluorination process, thereby positioning itself as a major player in the global phosphate market [2].

8.6 Future work and recommendations

While this study successfully demonstrated the potential for thermal defluorination of Central Kyzylkum phosphorites, further research is needed to optimize the process for large-scale industrial application. Specifically, future studies should focus on:

- Exploring the effects of additives like SiO₂ to further enhance fluorine volatilization.
- Investigating alternative heat sources, such as microwave or solar energy, to reduce energy consumption.
- Developing hybrid processes that combine thermal and chemical methods to improve efficiency.
- Assessing the economic feasibility of scaling up the process, including detailed cost-benefit analyses and environmental impact assessments.

Additionally, pilot-scale experiments are recommended to validate the laboratory-scale findings and ensure the process can be applied at industrial scales with consistent results.

9 Conclusion

The thermal defluorination of phosphorites from the Central Kyzylkum region is a highly effective method for producing environmentally safe and agriculturally beneficial phosphates. The significant reduction in fluoride content, combined with enhanced phosphorus solubility, positions these phosphates as superior fertilizers compared to untreated alternatives. Furthermore, the economic benefits of utilizing local resources outweigh the energy costs associated with the thermal process, making it a viable option for sustainable agriculture in the region. Future studies should focus on optimizing the process parameters to further reduce energy consumption while maintaining high defluorination efficiency and phosphorus availability.

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