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PHYSICO-CHEMICAL CHARACTERIZATION OF PHOSPHATIC WASTE: STATISTICAL APPROACH AND EFFICIENT VALORIZATION REMEDIES (ALGERIA)

Purpose. A detailed study of phosphatic dry waste from Algerian Djebel Onk mine. The ore extraction by dry process generates two wastes: coarse dry rejection +2 and +1 mm (named CDR) and fine reject from the turbo ventilate selector (named TSV).

Methodology. Several techniques are used in order to characterize the representative samples taken from the study area, including X-ray fluorescence spectrometry (XRF) for chemical assessments and also advanced statistical analysis using principal component analysis, X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), thermogravimetric analysis and differential scanning calorimetry (TGA/DSC), as well as scanning electron microscopy coupled with energy dispersive spectroscopy (SEM-EDS).

Findings. The obtained results indicates that dry wastes are mostly composed of hydroxyapatite and fluorapatite associated to dolomite, calcite, quartz and muscovite. Chemical assessments using XRF and advanced statistical analysis shows that the phosphate dry wastes display a composition similar to raw phosphate, although the mineral association makes the difference: in the case of the coarse reject Na, Sr, and S are related to the apatitic phase, while for fine rejection labeled TSV, only strontium is associated, alongside the clay phase containing Ti, Fe, Cr, Zn, etc. Supporting this findings, significant levels of CaO and P_2O_5 content exceeding 46.33 and 25.41 % (wt.%) respectively for TSV are found. Conversely, CDR rejections contained 45.45 % CaO and 24.78 % P_2O_5, alongside predominant apatitic minerals (hydroxyapatite and fluorapatite) are most present in CDR 0.25 mm fraction with almost 29 (wt.%) of P_2O_5.

Originality. The study presents valuable insights for the efficient use and valorization of phosphate dry waste materials based on statistical approach in order to predict the mineral composition.

Practical value. The phosphorus-rich composition of the phosphate dry wastes suggests potential for valorization. For instance, the 0.25 mm fraction of CDR could be valorized directly with appropriate screening processes while fine TSV particles contain more than 40 % of fraction higher than sieve mesh (80 μm) which need additional screening to prevent loss of concentrated ore P_2O_5. The potential utilization of different samples in construction materials or as soil fertilizers is also highlighted. The fixation of minor elements is linked to the liberation of the clay matrix in certain samples, offering opportunities for further processing and value extraction.

Keywords: *mining wastes, tailings, phosphate ore processing, turbo ventilated selector, valorization of phosphate waste, Djebel-Onk deposits*

Introduction. For several years, mining industry has been emphasizing the critical importance of a sustainable practices of extraction and treatment methods; these operations generate a huge quantity of wastes such as waste rocks, tailings and sludge produced after milling and ore beneficiation [1]. For instance, to produce one ton of phosphate in Florida (USA), the processes engender over one ton of waste-clay, in the average of 20 million tons per year [2]. This sort of mine waste has several environmental impacts that take years to rectify. However, mine tailings comprise significant component which can be valorized and integrated towards beneficiated recovery, others are giving rise to a common environmental issues as acid mine drainage (AMD) caused by sulfides and sulfosalts with concentrations higher than the existing environmental criteria [3, 4]. For other cases the oxidation of neutralizing minerals (e.g. carbonates) by exposure to atmospheric conditions (weathering), leading to circumneutral drainage effluent named contaminated neutral drainage (CND) [2, 5, 6]. The mining drainage does not only lead to the contamination of the environment, but also to the degradation of biodiversity and damage to the ecological system [7]. The contamination from mining activities persists as a matter of global attention [8]. The phosphorites ores are considered as one of the most important raw materials that are highly extracted (220 million tons of mine production in 2023 [9]). Phosphate mining and beneficiation industry is constantly evolving to meet the growing demand of phosphate ore in agriculture sector as fertilizer thereby securing food production for the global population [10]. Industries involved in phosphate mining and processing and the associated waste by-products, remain a pertinent area of scientific research today with the objective of valorizing their wastes, thus protecting the environment [11, 12]. Phosphate ore enrichment techniques are utilized to distinguish and remove the gangue minerals, isolating them from the economical valuable phosphate. Sedimentary phosphate ores, the major impurities are in calcite and/or dolomite and silica. Whereas, for the igneous and metamorphic phosphate ores the main gangue materials are carbonates (calcite, dolomite, siderite, and ankerite), magnetite, sulfides, pyroxenite, foskorite, nepheline syenite, etc. [13, 14].

Several methods are employed to enhance the low-grade phosphate ore into a product of marketable quality. The effective beneficiation methods depend on the ore type, phosphate content, textural properties of the phosphate (e.g., liberation of apatite and the gangue minerals, apatite-gangue mineral associations), and the cost associated to the method used [15]. Treatment processes for phosphate ore extraction involve both basic mechanical preparation and advanced methods like flotation and leaching on large scale. Mechanical techniques include crushing, grinding, and screening to reduce or eliminate the gangue materials. In addition, pre-enrichment procedures involving attrition, scrubbing, washing, and desliming are used to eliminate clays and fine silicates [16]. Furthermore, for the best phosphate ore beneficiation several methods are widely used such as flotation, calcination, electromagnetic separation, leaching, gravity separation, and magnetic separation [17]. These techniques allow the reduction of impurities considerably for phosphoric acid production [18]. Beneficiation techniques employed to valorize low-grade phosphate ore, are chosen based on their suitability for phosphate mine waste rock. Due to the environmental risks assessed to the accumulation of minerals waste this work aims to explore a potential solution to the phosphate reject obtained from the dry way process by studying the chemical, mineralogical and physical proprieties characterizing the phosphate dry wastes and the raw phosphate product. To enhance clarity, a detailed analysis was conducted on each individual reject, focusing on its dimensional distribution. The objective was to explore the possibility of reintegrating these waste materials, either in their entirety or in part, into the process.

Materials and methods. ***Studied area.*** The Kef-Essnoune deposit is a part of the phosphate basin of Djebel Onk, which is located about 100 km south of Tebessa city, 20 km from the Algerian-Tunisian border and 340 km from Annaba's port facilities. With 2.2 billion tons of reserves and a mine production of about 1.8 MT for both 2022 and 2023 [9].

Ore treatment process. Various classification methods including crushing, screening, scrubbing, attrition, desliming, washing, and grinding are employed to concentrate phosphate during the primary stage. Crushing and screening processes exploit the difference in friability among the associated gangue, phosphate minerals, and the cementing matrix comprise of silicates and carbonates [19]. The mechanical fragmentation consists of crushing at 0–200 mm using gyratory cone crusher "BABBITLESS" 100 t/h of the run-of-mine, followed by grinding using a hammer mill (TRIMAN) 300 t/h with an outlet of 20 mm, then screening using vibrating resonance screens (WEDAG) 300 t/h with a mesh size of 15 mm, where the initial humidity typically falls between 3 and 7 %, generating the first refusal wastes named (R + 15 mm) while the material that passes through is processed in two parallel lines (dry and wet ways) according to the process represented in Fig. 1.

Dry way installation is designed to obtain a dry concentrate with less than 1 % of humidity and P_2O_5 in the average of ~28.5 % (Fig. 2). This method involves processing 2/3 of the total quantity of phosphate ore supplied (i. e., <15 mm fraction) that is issued from the mechanical preparation. After drying in a furnace system in order to eliminate the fine part of silica and to achieve fluidization and reach a humidity of 1 %, a screening

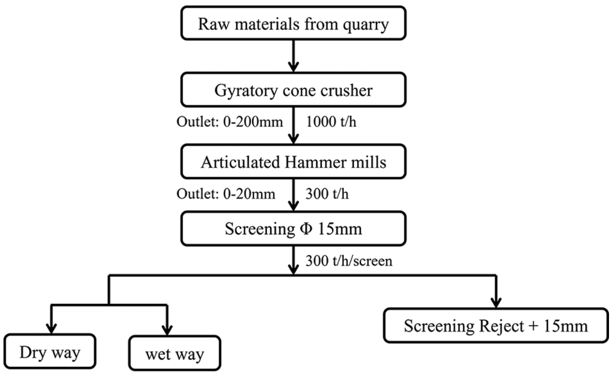


Fig. 1. Mechanical processing of phosphate rocks of Djebel-Onk mine

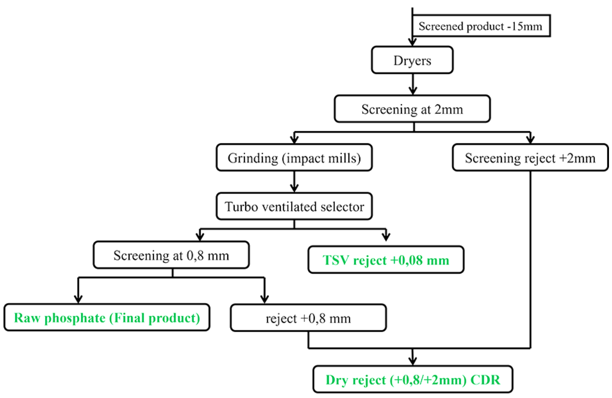


Fig. 2. Dry way flow sheet processing treatment

process is carried out at 2 mm size to eliminate the majority of coarse refusal (+2 mm). The passer is grounded by a hammer mill to remove some of the gangue matrix attached to phosphatic grains. Subsequently, separation is done using an air classifier (ventilate selector) with a size of 0.08 mm to eliminate fines (–0.08 mm) from the lower grade material. Following that, screening with 0.8 mm size is required to eliminate the larger particles (+0.8 mm). The fraction below 0.8 mm is the final concentrate, with P_2O_5 = ~29 wt. % yielding grades.

Studied materials. Flow sheet represented in Fig. 2, label the samples during phosphate treatment process. The studied samples are collected from the dry way (DWR; total of 02 samples).

Comprehensively, wastes obtained from the dry way were sampled from the turbo ventilate selector (–0.08 mm) named TSV, screening at 0.8 mm generate two coarse dry refusal (DR + 0.8) and 2 mm (DR + 2) are collected from the common conveyor (sample named CDR) and the raw phosphate (final product) from the same treatment way named RP. The samples were collected from different position in the treatment process each 30 min for 3 days and homogenized (by quarter split) next dried at room temperature for 7 days and stored in closed containers. The samples are then sieved according to the way standard EN 933-2 recommends; for the particle size analysis, the following series of sieves in (mm): 0.063, 0.125, 0.25, 0.50, 1, 2 were used.

Analysis methods. The raw materials are characterized using X-ray fluorescence (Burker S8 TIGER) to define its chemical composition while its mineralogical composition is obtained using X-ray diffraction (XRD) by a PANalytical EMPYREAN series 03 diffractometer with Cu Kα radiation (0.154186 nm) operating in a range of 5 to 80 (2θ). Identification and quantification of existed phases are performed by X'Pert Highscore Plus and Match software. The thermal gravimetric analysis (TGA) is carried out starting from air atmosphere temperature to 1,100 °C with a heating rate of 10 °C/min using PERKIN Elmer STA 8000. Fourier Transform Infrared spectroscopy (FTIR) is measured between 400 and 4,000 cm^{-1} with a resolution of 4 cm^{-1} by Nicolet IS5 spectrometer. The SEM images are obtained using a scanning electron microscope (SEM) JSM-7200F. Specific Surface Area by means of the method of BET using an ASAP 2020 Plus Version 2.00 equipment and apparent density was determined following (NA 255/1990) standards. While particle size distribution is measured by laser particle size analyzer HORIBA partica LA-960.

Results and discussion. ***Particle size distribution.*** The weight yield of each sieve for the dry way rejects sample CDR (Table 1) shows that the refusal of 2mm sieve represents a quantity of 17 % while the most dominant fractions are (0.25 and 1.25 mm) with 33.41 and 22.49 % respectively, whereas remaining particle size fractions are minimally present with yields between 8–5 % which is justified by the uniformity coefficient of 3.7.

For TSV the entire sample distribution is less than 0.25 mm (yielding of 0.12 %). 40.24 and 48.41 % are for the 0.125 and 0.063 mm sieve respectively qualifying the major fractions (uniformity coefficient = 20.8) (Table 2). The bottom of the sieve contains the fraction less than 0.063 mm which represents 11 %. Particles less than 0.063 mm are analyzed by laser distribution the results and are illustrated in Fig. 3, *a* and Table 3.

Table 1

Weight yielding of coarse dry reject CDR

CDR	Sieve (mm)	Wt.%
Weight yield of each sieve (wt. %)	2	17.51
	1	6.73
	0.5	5.30
	0.25	33.41
	0.125	22.49
	0.063	8.76
	0	5.80
Uniformity coefficient	3.7	
Density	2.17	

Table 2

Weight yielding of fine particles TSV

TSV	Sieve (mm)	%
Weight yield of each sieve (wt. %)	0.25	0.12
	0.125	40.27
	0.063	48.41
	0	11.20
Uniformity coefficient	20.8	
Density	2.08	

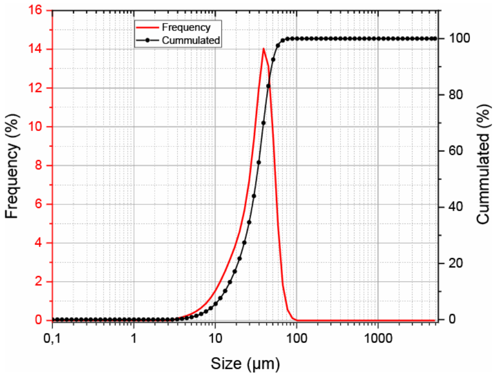
Table 3

Particle size distribution

Granulometry by laser	Median diameter µm	Average diameter µm	D10 µm	D90 µm
CDR	25.09	26.51	11.71	43.30
Fine TSV	32.02	31.85	13.11	49.62

A specific surface area (SSA) measurement of phosphate waste rock, by the Brunauer-Emmett-Teller, gives 24.9535 m^2/g for TSV and 23.6213 m^2/g for CDR, indicating that natural phosphate has a low SSA compared with synthetic apatite with values superiors of 120 m^2/g [20] while the Langmuir Surface Area for fine particles rejects TSV and CDR are: 112.0436 and 95.7703 m^2/g respectively. The isotherm of adsorption-desorption of nitrogen with the phosphate rock is illustrated in Fig. 4, which is of type IV (mesopores et micropores) according to the Brunauer classification. Single point adsorption total pore volume of pores less than 40.3122 nm diameter at P/Po = 0.95 is 0.045 cm^3/g for TSV and 0.037 cm^3/g for coarse dry rejection (CDR).

Chemical composition. The chemical composition of raw phosphate and the phosphate waste rocks for both main sample (Table 4) and by particle size range is summarized in (Tables 5 and 6). The principal constituents of these samples are the apatitic phase to which other clay and siliceous mineral, sulphates, carbonates and organic matter are associated. Other elements with negligible amounts were detected.



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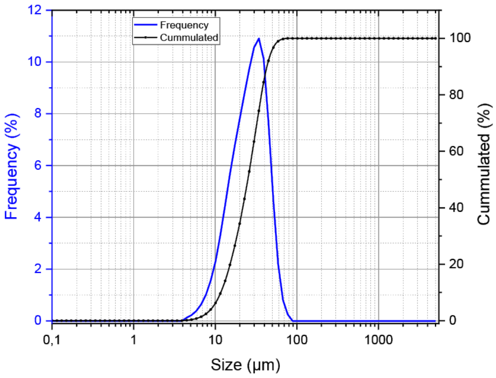

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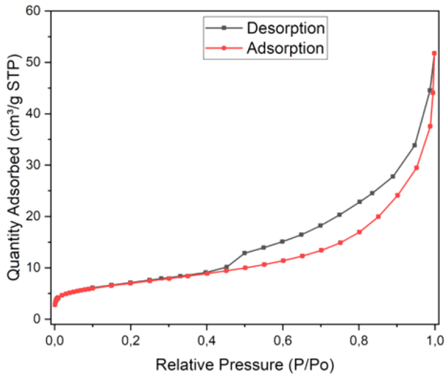
Fig. 3 .Particle size distribution:
a – fine particles TSV; b – dry rejects CDR



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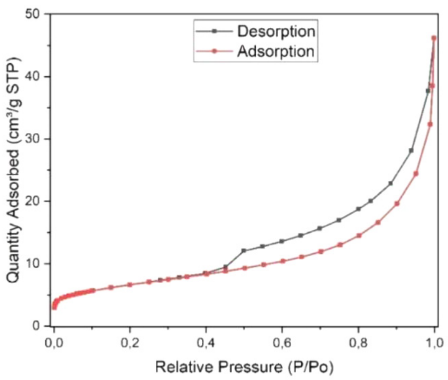

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Fig. 4. Isotherms of adsorption and desorption by nitrogen of phosphate:
a – TSV; b – CDR rejects

Table 4

X Ray fluorescence results of the main samples

	RP	CDR	TSV
SiO_2	2.21	4.44	4.09
Al_2O_3	0.45	0.89	0.81
Fe_2O_3	0.41	0.58	0.51
CaO	48.92	45.45	46.33
MgO	0.84	3.18	3.11
SO_3	2.98	2.15	2.16
K_2O	0.10	0.16	0.15
Na_2O	1.11	0.91	0.89
P_2O_5	29.46	24.78	25.41
TiO_2	0.04	0.05	0.04
Cr_2O_3	0.03	0.04	0.03
Mn_2O_3	0.01	0.01	0.01
ZnO	0.01	0.02	0.02
SrO	0.26	0.23	0.23
LOI	10.30	15.46	14.70

Table 5

X Ray fluorescence results of TSV: samples by grade size

Sieve (µm)	TSV 125	TSV 63	TSV < 63
SiO_2	4.16	3.02	7.88
Al_2O_3	0.79	0.58	1.56
Fe_2O_3	0.47	0.39	0.70
CaO	45.54	47.65	42.71
MgO	3.63	2.37	3.32
P_2O_5	24.06	26.85	22.79
SO_3	2.36	2.57	2.24
K_2O	0.06	0.04	0.28
Na_2O	0.76	0.70	0.81
TiO_2	0.04	0.03	0.05
Cr_2O_3	0.04	0.04	0.05
ZnO	0.02	0.02	0.02
SrO	0.21	0.24	0.21
Mn_2O_3	0.01	0.00	0.01
LOI	16.09	13.38	15.50

Mineralogical composition. The XRD patterns pastes of CDR and TSV and its fractions compared with RP are presented in Fig. 5, *a*. As revealed in the figure, five types of well-crystallized phases, including Dolomite, calcite, quartz, hydroxyapatite and fluorapatite were clearly identified in XRD pattern. And the most dominant phases are the apatitic ones. The CDR grading size diffractogram (Fig. 5, *b*) shows the existence of the same major phases and the appearance of clay (9.80°2θ) in fine fraction (<0.063 mm), the coarse particles contain a more dolomitic gangue (30.92–41.15–50.53 (°2θ)) and quartz (21.04–26.80–55.01 (°2θ)) and calcite. The majority of the intense lines attributed to the apatitic phases are in the refusal of the sieve 0.25 mm which is similar to the raw phosphate RP. As shown in X-ray dif-

Table 6

X Ray fluorescence results of CDR: samples by grade size

Sieve (mm)	CDR 2	CDR 1	CDR 0.5	CDR 0.25	CDR 0.125	CDR 0.063	CDR <0.063
SiO_2	6.47	5.47	4.00	2.15	2.63	7.52	15.59
Al_2O_3	1.06	1.17	0.92	0.66	0.59	1.63	3.25
Fe_2O_3	0.56	0.58	0.52	0.45	0.38	0.71	1.36
CaO	42.22	43.09	46.13	49.05	47.44	38.63	34.55
MgO	5.29	4.74	2.79	0.97	2.25	7.16	5.04
P_2O_5	19.07	20.43	24.91	29.25	26.89	16.19	16.22
SO_3	1.89	2.01	2.34	2.74	2.51	1.62	1.57
K_2O	0.16	0.16	0.13	0.14	0.11	0.30	0.60
Na_2O	0.76	0.81	0.98	1.09	1.01	0.65	0.71
TiO_2	0.05	0.06	0.05	0.04	0.03	0.06	0.09
Cr_2O_3	0.04	0.05	0.04	0.32	0.03	0.06	0.07
ZnO	0.02	0.02	0.02	0.02	0.02	0.02	0.03
SrO	0.18	0.19	0.23	0.26	0.25	0.15	0.18
Mn_2O_3	0.01	0.01	0.01	0.00	0.00	0.01	0.01
LOI	20.36	19.33	14.47	10.23	12.85	23.83	19.21

fractogram of the second examined sample, the main TSV (Fig. 5, *a*), and ranking size (Fig. 5, *c*), show that hydroxyapatite, fluorapatite and dolomite are the main mineralogical phases. Further, secondary minerals such as quartz, calcite and clay trace were identified. The results also show that for the grading size TSV 0.063 mm is highly composed of apatitic minerals and dolomite the later decrease with the decreasing of grading size so TSV 0.125 mm pattern show a high concentration of dolomite as well as the < 0.063 mm fraction reveal lower intensity of all precedent phases with the increasing of clay gangue.

Fourier-transform infrared spectroscopy analysis (FTIR). FTIR spectra were illustrated in Fig. 6. The re-

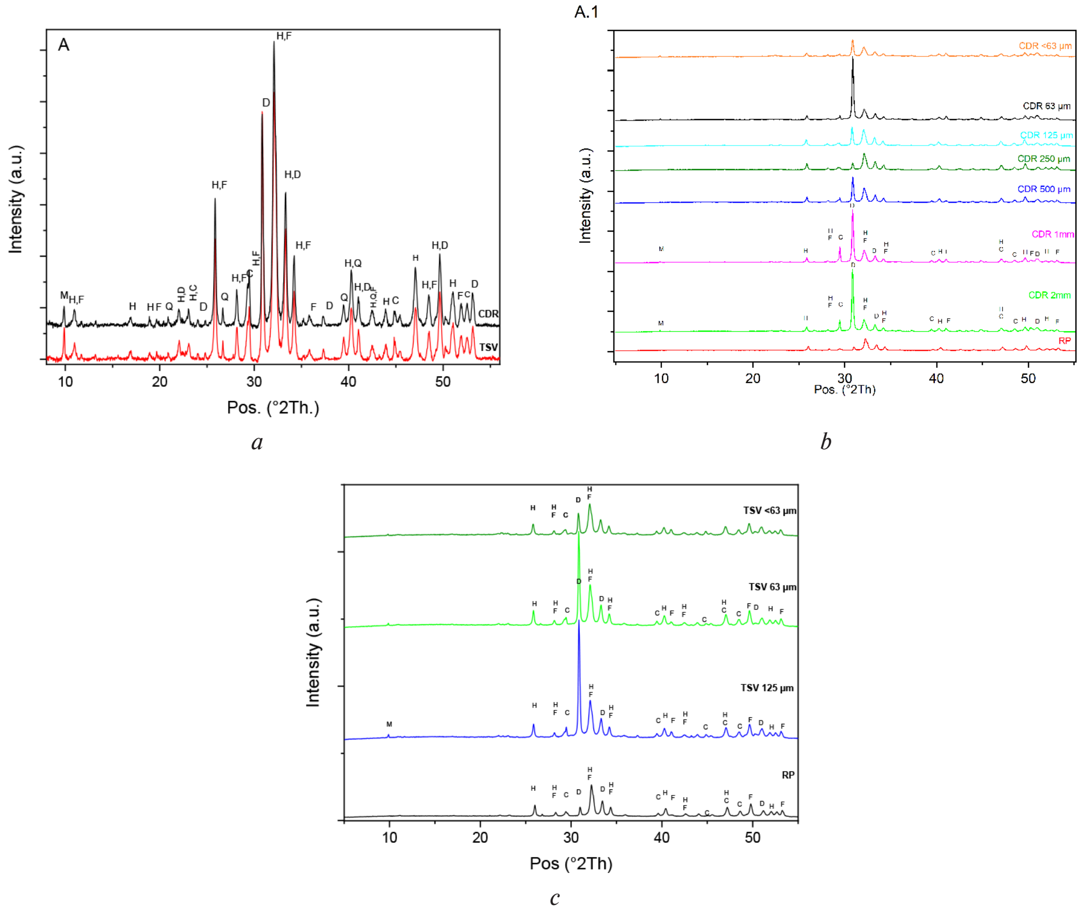


Fig. 5. XRD patterns of dry way reject samples:

a – CDR and TSV main samples; b – CDR grading size samples; c – TSV grading size samples. H – Hydroxyapatite, F – Fluorapatite, D – Dolomite, C – Calcite, M – Muscovite, Q – Quartz sults showed major intense bands in the range between 1,000 and 1,100 and at 473.72 cm^{-1} attributed to the phosphatic elements (PO_4^{-3}), (PO_4^{-2}) respectively. The intense band at 1,448 cm^{-1} is characteristic of ions CO_3^{2-} apatite, while the weak bands at 862 cm^{-1} correspond to the stretching mode of C=O existing in gangue carbonates, which is confirmed by presence of calcite identified in XRD patterns. The band observed at 2,534 cm^{-1} are attributed to C=O present in dolomite phase. Moreover, the water of constitution in apatitic minerals (e.g. $Ca_3(PO_4)_2H_2O$) is highlighted by the band observed at 3,444.76 cm^{-1}, which shows relatively strong intensity, and is attributed to the OH^- groups present in the studied samples.

Thermal properties analysis. Thermal behavior study of wastes phosphates rock was carried out using thermal gravimetric analysis (TGA) and Differential Scanning Calorimetry (DSC) from room temperature to 1,100 °C with a heating rate of 10 °C/min. (Fig. 7). The TGA curve of the Dry way phosphate wastes CDR indicates a first weight loss of 2.86 % between 25 and 322 °C corresponding to the desorption of humidity water and a loss of 0.65 % at 490 °C attributed to water of structural constitution dehydration. A second mass loss of 0.95 % between 500 and 630 °C corresponds to the elimination of organic matter. The last weight loss of 9.52 % between 630 and 773 °C and of 3.69 % from 773 up to 1,100 °C is attributed to the decomposition of mineral carbonates present in the phosphate (Fig. 1, *a*), whereas Thermogravimetric analysis (TGA) for the TSV reveals a mass loss of 1.69 % in the temperature range (ambient T – 309.8 °C) attributed to humidity water and constitutional water. Then a second mass loss of 1.59 % is observed between 309.8 and 600 °C attributed to the decomposition of organic matter. The carbonate decomposition is recorded in range from 600 to 1,084 °C with a mass loss of about 12 %. The DSC studies of all samples demonstrate the exothermic crystallization region location near 750 °C.

Scanning electron microscopy results. The SEM images of dry way wastes are shown in Fig. 8. The particles are distinguished from their matrix based on their shape. CDR samples (Fig. 8, *a*) comprise well-smoothed cylindrical coprolites Hydroxyapatite (HAp) sized in the average of 303 µm cemented in a carbonated aggregates matrix that contain dolomite in particular, clay and quartz are in small quantities. (Fig. 8, *a*). The TSV samples show homogeneous distribution of particles, with dimensions ranging between 50 and 110 µm, identified as phosphatic phase comprises rectangular grains (coprolites) and ovoid (pellets) sections (Fig. 8, *b*). Other particles are related to the presence of the organic residues and quartz grains. Coupled with the dispersive analysis in energy of X-rays (EDX) (Fig. 9) they display the presence of Ca, P, O, Si, C, F and traces of other elements. This observation completes the results found by XRD, FTIR and chemical analysis.

Statistical analysis of X-ray fluorescence results. The X-ray fluorescence results are discussed by static analysis by PCA (principal component analysis) and HAC (hierarchical ascending classification) illustrated in Fig. 10, for the HAC dendrogram for CDR, the interpretation is conducted based on 50 % similarity, which has yielded 02 groups: the first is represented by 02 subgroups (RP-CDR 0.25) and (CDR 0.125-CDR-DP0.5);

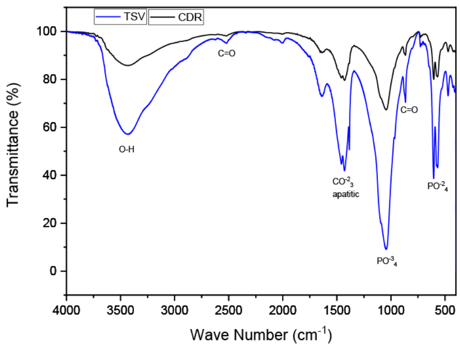


Fig. 6. FTIR curves of dry way rejects

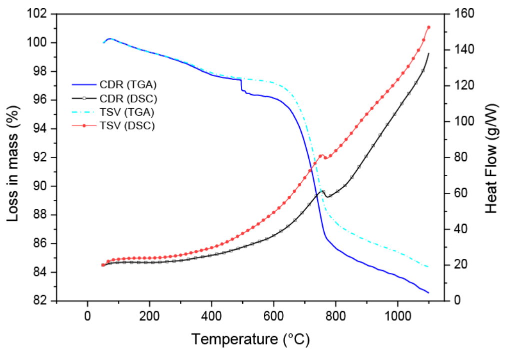
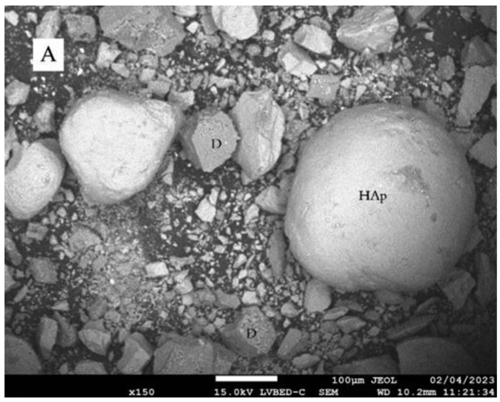


Fig. 7. The TGA/DSC curves for the dry way phosphate wastes



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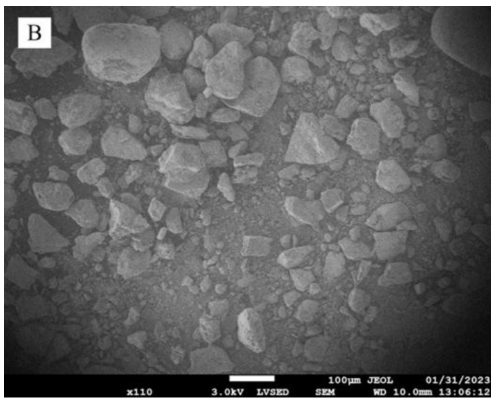

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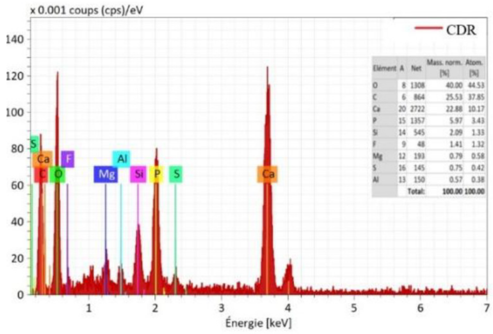
Fig. 8. SEM image of the dry way reject:
a – Dry way reject CDR; b – Fines particles TSV



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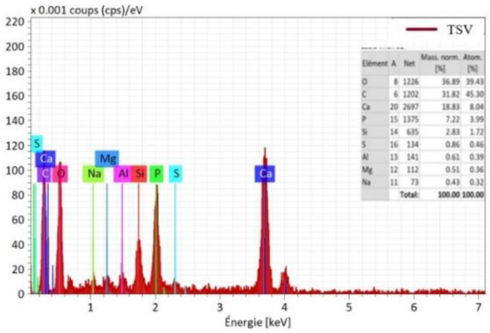


b

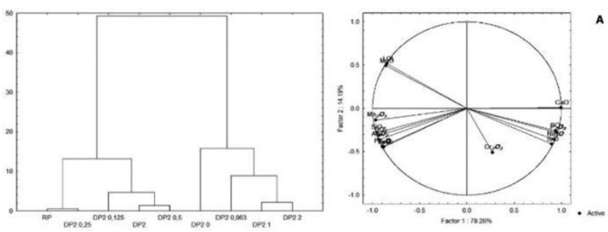
Fig. 9. EDX results:
a – CDR sample; b – TSV sample

the second subgroup is also represented by 02 subgroups which are CDR 0 (CDR 0.063 -CDR 1 and CDR 2 mm), The correlation circle analysis of the 15 variables, representing chemical components, demonstrates the existence of three distinct groupings revealing a direct relation between some elements as (SO_4, Na_2O, SrO) are attached to the existence of P_2O_5 and so for (Mn_2O_3, SiO_2, Al_2O_3, Fe_2O_3, TiO_2 and ZnO), which confirmed that most of minor elements are related to the clay matrix. The increase of LOI conduct to the liberation of MgO. These outcomes indicate that these groupings collectively account for 93.45 % of the total variance observed in the dataset. As for "TSV" samples, based on the Principal Component Analysis (PCA) results, it can be inferred that the first factor explains 74.6 % of the total variance, while the second factor accounts for 13 %. The correlation circle analysis supports the notion that there is a relationship between MgO and Na_2O component and the LOI (Loss on Ignition), whereas only SrO is attached to the apatitic phase (CaO-P_2O_5). The clay phase (SiO_2, Al_2O_3) contains also Cr_2O_3, Mn_2O_3, Fe_2O_3, TiO_2 and ZnO. According to HCA, for 50 % of similarity there are three (04) main groups for fine particles rejects TSV: RP; TSV0; TSV63 and (TSV-TSV125 μm).

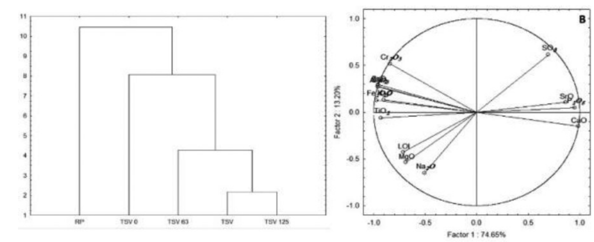
Conclusion. This work was to conduct a detailed structural and physical-chemical study characterizing the Algerian phosphate waste rock from the dry way process of Djebel-Onk deposits. The chemical results by X-Ray Fluorescence (XRF) and statistical analysis reveal that the phosphate dry way wastes have a similar composition to the raw phosphate by containing large amounts of CaO, P_2O_5 more than 46.33 and 25.41 (wt.%) respectively for fines particles named TSV, while CDR rejections contain 45.45 % CaO and 24.78 % P_2O_5. Corresponding to the dominant phases of apatitic minerals (hydroxyapatite and fluorapatite) and dolomite. MgO, SiO_2 as major elements; Fe, Ni, Zn, Ti, Mn are trace elements standing in low proportions. According to statistical results (PCA), these elements are related to the clay matrix besides demonstrating that some elements such as (SO_4, Na_2O, SrO) are attached to the existence of P_2O_5. For TSV, the phosphatic release mesh is TSV 0.063 with a weight yield of 48.41 % containing 26 % of P_2O_5, although PCA results determining correlations between different elements predict that only SrO is related to the apatitic phase (CaO-P_2O_5) and the clay phase (SiO_2-Al_2O_3) contains Cr_2O_3, Mn_2O_3, Fe_2O_3, TiO and ZnO.

The mineralogical composition revealed five major mineral phases: dolomite, calcite, apatitic-phases and quartz, present in all samples and grading samples with CDR 0.25 and TSV63 as high intensity with apatitic phases.

In addition to chemical and mineralogical composition, the behavior of particulate materials is often dominated by the physical properties of the constituent particles. By far the most physical property is particles size, which has a direct influence on materials properties such as: reactivity or dissolution rate, stability in suspension, packing density and porosity, etc. In our case measuring particles size for the phosphate dry way treatment rejects revealed that the variation of particles size distribution improves physical properties especially specific area and porosity. Therefore, significant exposure of organic material and carbonates to the exterior results in a large specific surface area of the finished product, and a decrease in density, due to porosity contributing along with volume mass (density) in the laws of matter conservation. This limits the sedimentation rate of phosphate pulp or slurry during the production of phosphoric acid, with the absence of sticking and the formation of aggregates on the reactor surfaces (as for CDR 0.063; TSV 125: augmentation of LOI while MgO is in the highest value). The examination using Scanning Electron Microscopy (SEM) indicates that the samples comprised mainly of coprolites and pellets ex-



a



b

Fig. 10. Statistic analysis for chemical results:
a – CDR sample; b – TSV sample

hibit higher concentrations of P_2O_5 compared to the surrounding carbonated matrix (especially dolomite) and quartz in the samples. The phosphate dry wastes, characterized by TGA/DSC and FTIR, show a phosphorus-rich composition with carbonate-apatite being the primary mineral phase. However, there is a similar variability in the composition of the major elements between the two samples CDR and TSV. Additionally, the TGA findings from this study reveal that thermophysical and chemical factors interact with each other. The calcination process may involve these parameters, playing a critical role in the enrichment mechanisms and the production of an improved product, which requires careful management.

SEM analysis reveals that the examined samples, largely composed of coprolites and pellets, have P_2O_5 concentrations that are higher in comparison to those found in the adjacent carbonate matrix, particularly dolomite, and quartz within the samples. The phosphate-containing dry wastes, studied through TGA/DSC and FTIR techniques, display an abundance of phosphorus, with carbonate-apatite identified as the major mineral phase. Nevertheless, a similar degree of variation is observed in the elemental composition between sample CDR and sample TSV. The TGA data from this investigation also present a carbonate destruction at ~800 °C and the liberation of apatitic phases.

To conclude, over than 40 % of the fine particles rejects TSV are having dimension superior than the sieve 0.08 mm of treatment process, which may cause the loss of concentrated ore P_2O_5 needing a double screening to preserve it. While for CDR the phosphatic release mech is 0.25 with a weight yield of 33.41 % having an identical composition as the raw phosphate RP so it can be valorized directly by the installation of two screens with a mesh size 0.5 and 0.25 mm respectively as a protentional remedy while CDR 2 mm and CDR 1 mm and main TSV sample can be used directly in the production of construction materials or as a direct soil fertilizes. The fixation of the minor elements such as Fe, Cr, Ti, Sr, etc. are related to the liberation of the clay matrix (CDR < 0.063 and TSV < 0.063).

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References.

1. Makhathini, T. P., Bwapwa, J. K., & Mtsweni, S. (2023). Various Options for Mining and Metallurgical Waste in the Circular Economy: A Review. *Sustainability, 15*(3), 2518. https://doi.org/10.3390/SU15032518

2. Eskanlou, A., & Huang, Q. (2021). Phosphatic waste clay: Origin, composition, physicochemical properties, challenges, values and possible remedies – A review. *Minerals Engineering, 162*, 106745. https://doi.org/10.1016/j.mineng.2020.106745

3. Mafra, C., Bouzahzah, H., Stamenov, L., & Gaydardzhiev, S. (2020). Insights on the effect of pyrite liberation degree upon the acid mine drainage potential of sulfide flotation tailings. *Applied Geochemistry, 123*, 104774. https://doi.org/10.1016/j.apgeochem.2020.104774

4. Ait-Khouia, Y., Benzaazoua, M., & Demers, I. (2021). Environmental desulfurization of mine wastes using various mineral processing techniques: Recent advances and opportunities. *Minerals Engineering, 174*, 107225. https://doi.org/10.1016/j.mineng.2021.107225

5. Plante, B. (2010). Evaluation des principaux facteurs d'influence sur la prédiction du drainage neutre contaminé [Université du Québec]. Retrieved from https://scholar.google.com/scholar_lookup?title=%C3%89valuation%20des%20principaux%20facteurs%20d%27influence%20sur%20la%20pr%C3%A9diction%20du%20drainage%20neutre%20contamin%C3%A9&author=B.%20Plante&publication_year=2010

6. Mayes, W. M., Potter, H. A. B., & Jarvis, A. P. (2009). Novel approach to zinc removal from circum-neutral mine waters using pelletised recovered hydrous ferric oxide. *Journal of Hazardous Materials, 162*(1), 512-520. https://doi.org/10.1016/J.JHAZMAT.2008.05.078

7. Dold, B. (2017). Acid rock drainage prediction: A critical review. *Journal of Geochemical Exploration, 172*, 120-132. https://doi.org/10.1016/j.gexplo.2016.09.014

8. Khelifi, F., Caporale, A. G., Hamed, Y., & Adamo, P. (2021). Bioaccessibility of potentially toxic metals in soil, sediments and tailings from a north Africa phosphate-mining area: Insight into human health risk assessment. *Journal of Environmental Management, 279*, 111634. https://doi.org/10.1016/j.jenvman.2020.111634

9. Mineral commodity summaries 2024 (2024). https://doi.org/10.3133/mcs2024

10. Karunanithi, R., Szogi, A. A., Bolan, N., Naidu, R., Loganathan, P., Hunt, P. G., Vanotti, M. B., ..., & Krishnamoorthy, S. (2015). *Phosphorus Recovery and Reuse from Waste Streams*, (pp. 173-250). https://doi.org/10.1016/bs.agron.2014.12.005

11. Ettoumi, M., Jouini, M., Neculita, C. M., Bouhlel, S., Coudert, L., Taha, Y., & Benzaazoua, M. (2021). Characterization of phosphate processing sludge from Tunisian mining basin and its potential valorization in fired bricks making. *Journal of Cleaner Production, 284*, 124750. https://doi.org/10.1016/j.jclepro.2020.124750

12. Amrani, M., Taha, Y., Kchikach, A., Benzaazoua, M., & Hakkou, R. (2019). Valorization of Phosphate Mine Waste Rocks as Materials for Road Construction. *Minerals, 9*(4), 237. https://doi.org/10.3390/min9040237

13. Amar, H., Benzaazoua, M., Elghali, A., Hakkou, R., & Taha, Y. (2022). Waste rock reprocessing to enhance the sustainability of phosphate reserves: A critical review. *Journal of Cleaner Production, 381*, 135151. https://doi.org/10.1016/J.JCLEPRO.2022.135151

14. Abouzeid, A.-Z. M. (2008). Physical and thermal treatment of phosphate ores – An overview. *International Journal of Mineral Processing, 85*(4), 5984. https://doi.org/10.1016/j.minpro.2007.09.001

15. Elbendary, A., Aleksandrova, T., & Nikolaeva, N. (2019). Influence of operating parameters on the flotation of the Khibiny Apatite-Nepheline Deposits. *Journal of Materials Research and Technology, 8*(6), 5080-5090. https://doi.org/10.1016/j.jmrt.2019.08.027

16. Boujlel, H., Daldoul, G., Tlil, H., Souissi, R., Chebbi, N., Fattah, N., & Souissi, F. (2018). The Beneficiation Processes of Low-Grade Sedimentary Phosphates of Tozeur-Nefta Deposit (Gafsa-Metlaoui Basin: South of Tunisia). *Minerals 2019, 9*(1), 2. https://doi.org/10.3390/MIN9010002

17. Ruan, He, & Chi (2019). Review on Beneficiation Techniques and Reagents Used for Phosphate Ores. *Minerals, 9*(4), 253. https://doi.org/10.3390/min9040253

18. El Ouardi, E. M., Zeroual, A., Khallouq, K., Darfi, S., & Jedaa, A. (2020). Impact of washing followed by calcination on the quality of bouchane phosphate of Morocco. *International Journal of Design and Nature and Ecodynamics, 15*(4), 555-563. https://doi.org/10.18280/IJDNE.150413

19. Guo, F., & Li, J. (2010). Separation strategies for Jordanian phosphate rock with siliceous and calcareous gangues. *International Journal of Mineral Processing, 97*(1-4), 74-78. https://doi.org/10.1016/j.minpro.2010.08.006

20. Bachouâ, H., Othmani, M., Coppel, Y., Fatteh, N., Debbabi, M., & Badraoui, B. (2014). Structural and thermal investigations of a Tunisian natural phosphate rock. *Journal of Materials and Environmental Science, 5*(4), 1152-1159.

Фізико-хімічна характеристика фосфатних відходів: статистичний підхід і заходи з ефективної переробки (Алжир)

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Мета. Детальне дослідження сухих відходів фосфату родовища Джебель-Онк Алжиру. Видобуток руди методом сухого збагачення призводить до утворення двох видів відходів: крупні сухі відходи із розміром частинок +2 і +1 мм (із назвою CDR) та дрібні відходи з турбовентиляційного сортувальника (із назвою TSV).

Методика. Із метою характеристики вибіркових зразків, взятих із досліджуваної ділянки, використовуються кілька методів, включаючи рентгенівську флуоресцентну спектрометрію (XRF) у хімічній оцінці, а також сучасний статистичний метод на основі аналізу головних компонентів, рентгенівську дифракційну спектрометрію (XRD), інфрачервону спектрометрію з Фур'є-перетворенням (FTIR), термогравіметричний аналіз і диференціальну скануючу калориметрію (TGA/DSC), а також скануючу електронну мікроскопію в поєднанні з енергодисперсійною спектрометрією (SEM-EDS).

Результати. Отримані результати показують, що сухі фосфатні відходи в основному складаються із гідроксиапатиту й фторапатиту, пов'язаних із доломітом, кальцитом, кварцом і мусковітом. Хімічна оцінка за допомогою XRF і розширеного статистичного аналізу показує, що сухі фосфатні відходи мають склад, схожий на сирий фосфат, хоча відрізняються за мінеральним складом: у випадку крупних відходів, Na, Sr та S пов'язані з апатитною фазою, тоді як для дрібних відходів, позначених як TSV, з нею пов'язаний лише стронцій, поряд із глинистою фазою, що містить Ti, Fe, Cr, Zn тощо. На підтвердження цього висновку виявлено значний вміст CaO і P_2O_5, що перевищує 46,33 і 25,41 % (мас.%) відповідно для TSV. Навпаки, відходи CDR містили 45,45 % CaO і 24,78 % P_2O_5, поряд із переважаючими апатитовими мінералами (гідроксиапатит і фторапатит), що найбільше присутні у фракції CDR 0,25 мм із майже 29 (мас.%) P_2O_5.

Наукова новизна. У дослідженні представлені цінні висновки щодо ефективного використання й валорізації сухих відходів фосфатів на основі статистичного методу прогнозування мінерального складу.

Практична значимість. Склад сухих відходів фосфатів, збагачений фосфором, свідчить про можливість їх ефективної переробки. Наприклад, фракція CDR розміром 0,25 мм може бути перероблена безпосередньо за допомогою відповідних процесів сортування, тоді як дрібні частинки TSV містять більше 40 % фракції, розмір якої перевищує розмір сита (80 мкм), що вимагає додаткового сортування для запобігання втрати концентрованої руди P_2O_5. Також підкреслюється потенційне використання різних зразків у будівельних матеріалах або як добриво для ґрунту. Фіксація мікроелементів пов'язана із вивільненням глинистої матриці в деяких зразках, що відкриває можливості для подальшої переробки й вилучення цінних речовин.

Ключові слова: *відходи гірничодобувної промисловості, хвости збагачення, переробка фосфатної руди, турбовентильований сортувальник, утилізація фосфатних відходів, родовище Джебель-Онк*

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