Caractérisations et voies de valorisation potentielles des stériles de phosphate

Amine el Mahdi **SAFHI**

En collaboration avec:

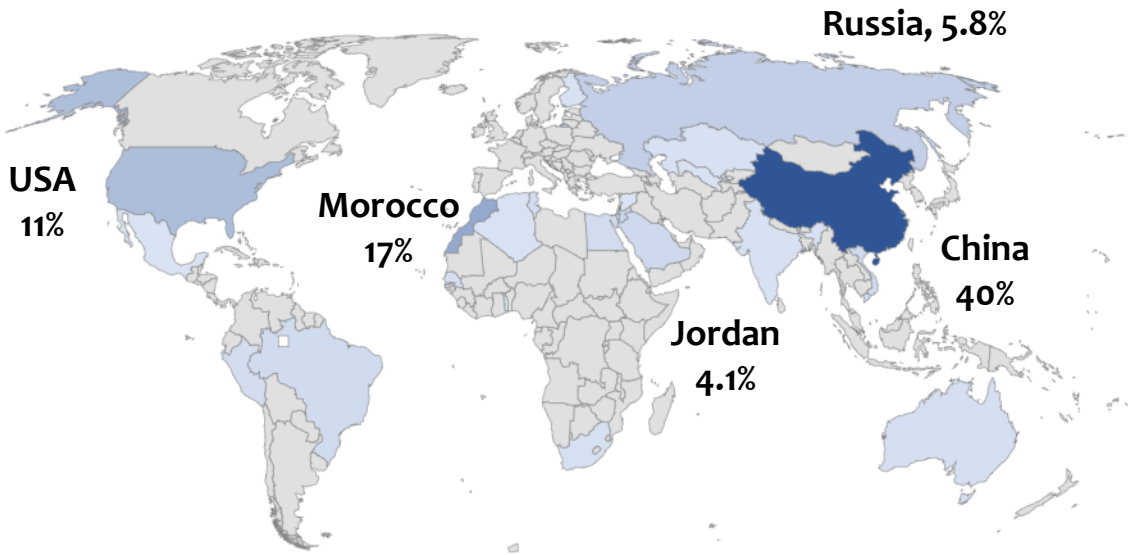
Hicham **AMAR**, Yahya **EL BERDAI**, Mustapha **EL GHORFI**, Yassine **TAHA**, Rachid **HAKKOU**, Muthanna **AL-DAHHAN**, Mostafa **BENZAAZOUA**

Outline of the presentation

- Introduction & research significance
- Materials properties
- Proposed strategy
- Potential uses of the by-products
- Conclusions & perspectives

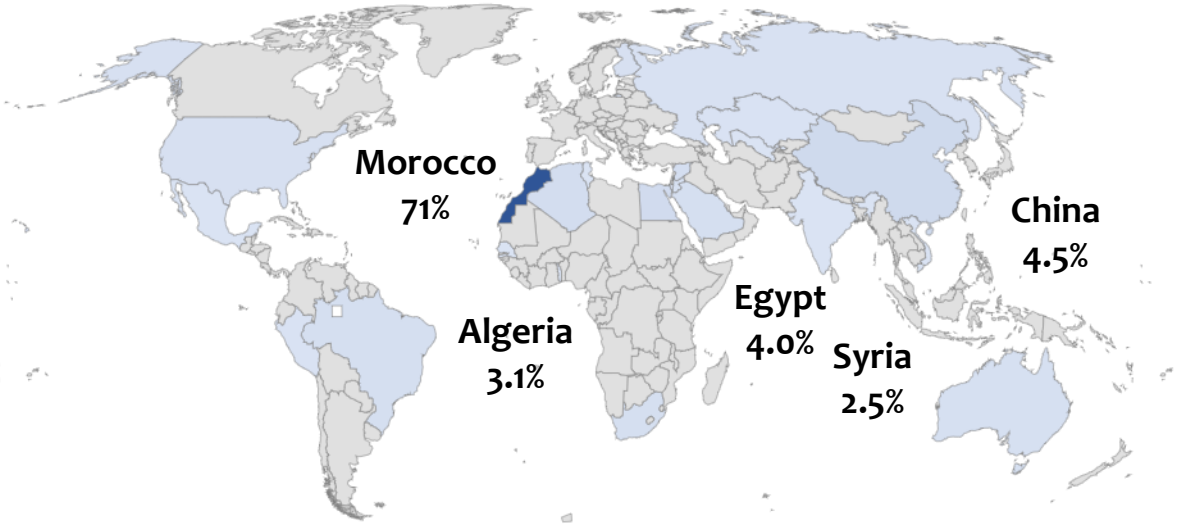
Phosphate: Rock deposits & Production

Worldwide Phosphate Production: 220 Million metric ton



6.	*Saudi Arabia*	*2.9%*
7.	*Brazil*	*2.5%*
8.	*Egypt*	*2.2%*
9.	*Vietnam*	*2.1%*
10.	*Peru*	*1.8%*

Worldwide Phosphate Reserve: 71 Billion metric ton

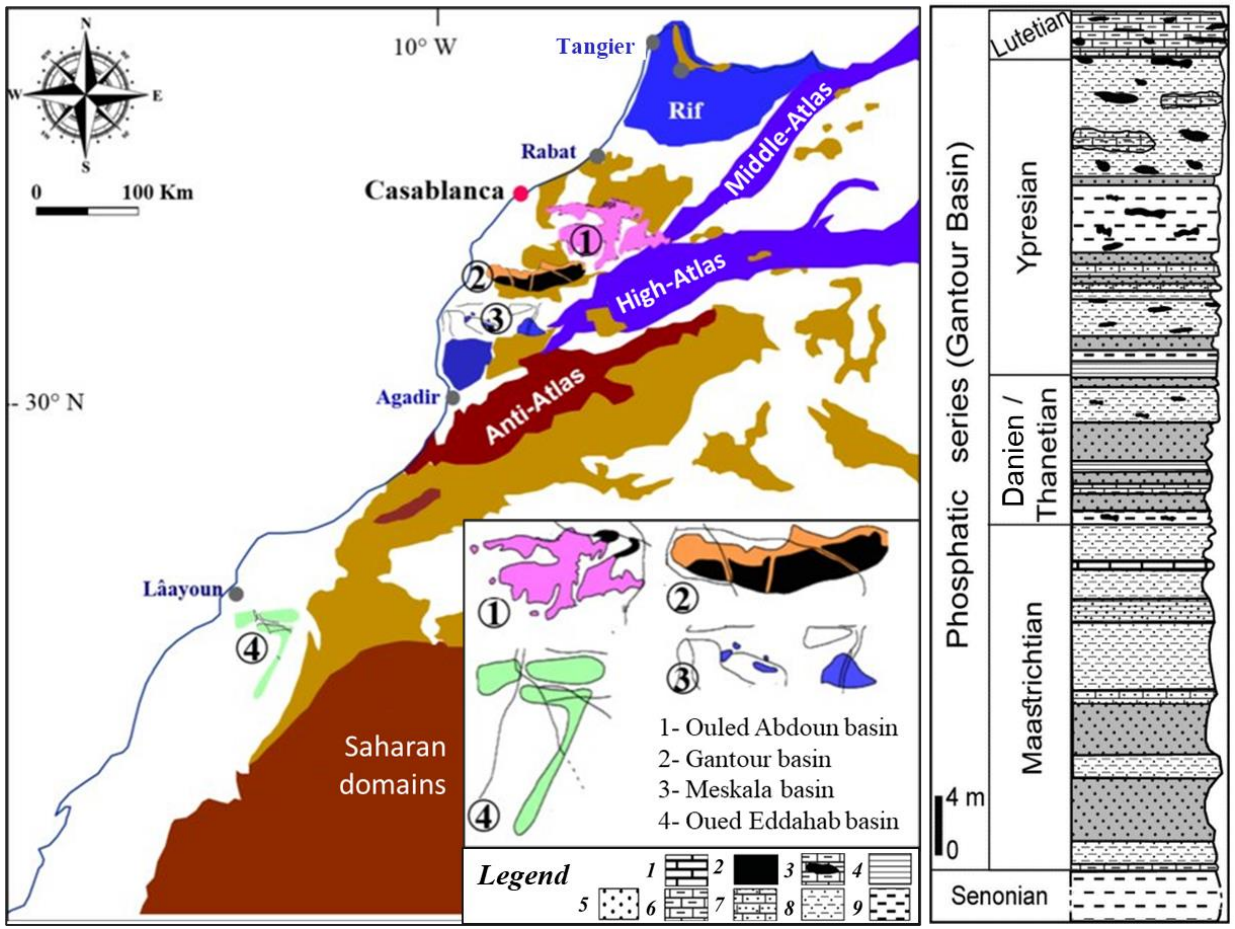


6.	*Brazil*	*2.3%*
7.	*South Africa*	*2.0%*
8.	*Saudi Arabia*	*2.0%*
9.	*Australia*	*1.6%*
10.	*USA*	*1.4%*

Mineral Commodity Summaries 2022. By: U.S. Geological Survey. DOI: 10.3133/mcs2022

Phosphate basins in Morocco

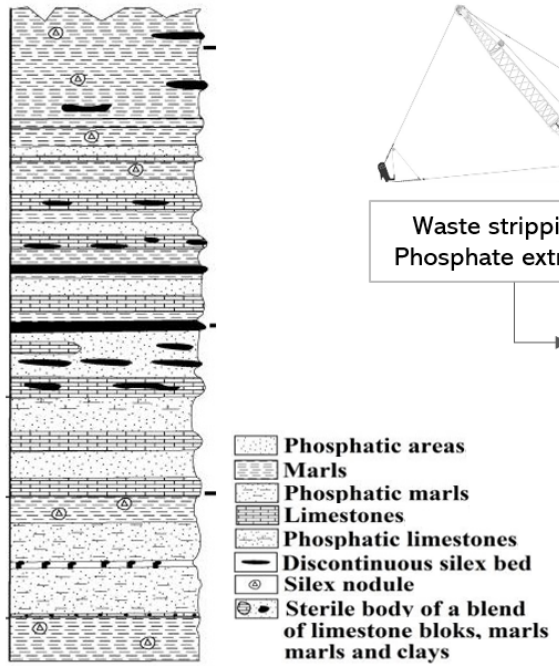
Phosphate mine waste rocks (PMWR): Marls, Limestone blocks, Flintstone, Clays, Silicates, etc.



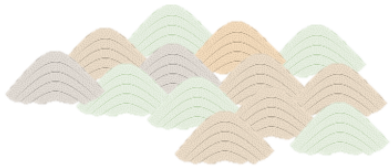
(El Haddi, 2014; Ihbach et al., 2020)

Legend of the lithologic column: 1) Limestone, 2) Flintstone, 3) Marley-silicious limestone, 4) Clay, 5) Uncemented phosphate, 6) Marley limestone, 7) Phosphatic limestone, 8) Phosphatic marl, 9) Marl

Phosphate extraction: Different waste streams



Waste rocks dumps



Waste stripping & Phosphate extraction

Phosphate extraction

Crushing and dry sieving (90mm)

- 90 mm

Dry sieving (30 x 15 mm)

Wet sieving (3.15 mm)

Washing (hydro-sizers and hydro-cyclones, 40µm)

Phosphate sludge

Flotation (40 – 160 µm)

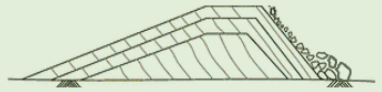
Froth tailings

Concentrated phosphate

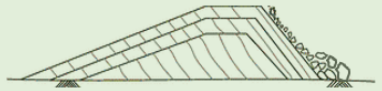
Chemical transformation (H2SO4)

Phosphogypsum (– 100 µm)

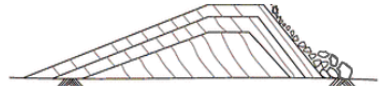
Destoning waste rocks piles (+90mm)



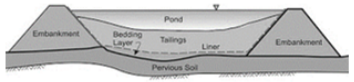
Screening waste rocks piles (+30mm – 90mm)



Beneficiation waste rocks piles (+2.5/3.15 mm)



Beneficiation tailings ponds (– 200 µm)



Phosphate Mine Waste Rocks (PMWR)

Taha et al., 2021, Towards Zero Solid Waste in the Sedimentary Phosphate Industry: Challenges & Opportunities. Minerals, 11, 1250. DOI: 10.3390/min11111250

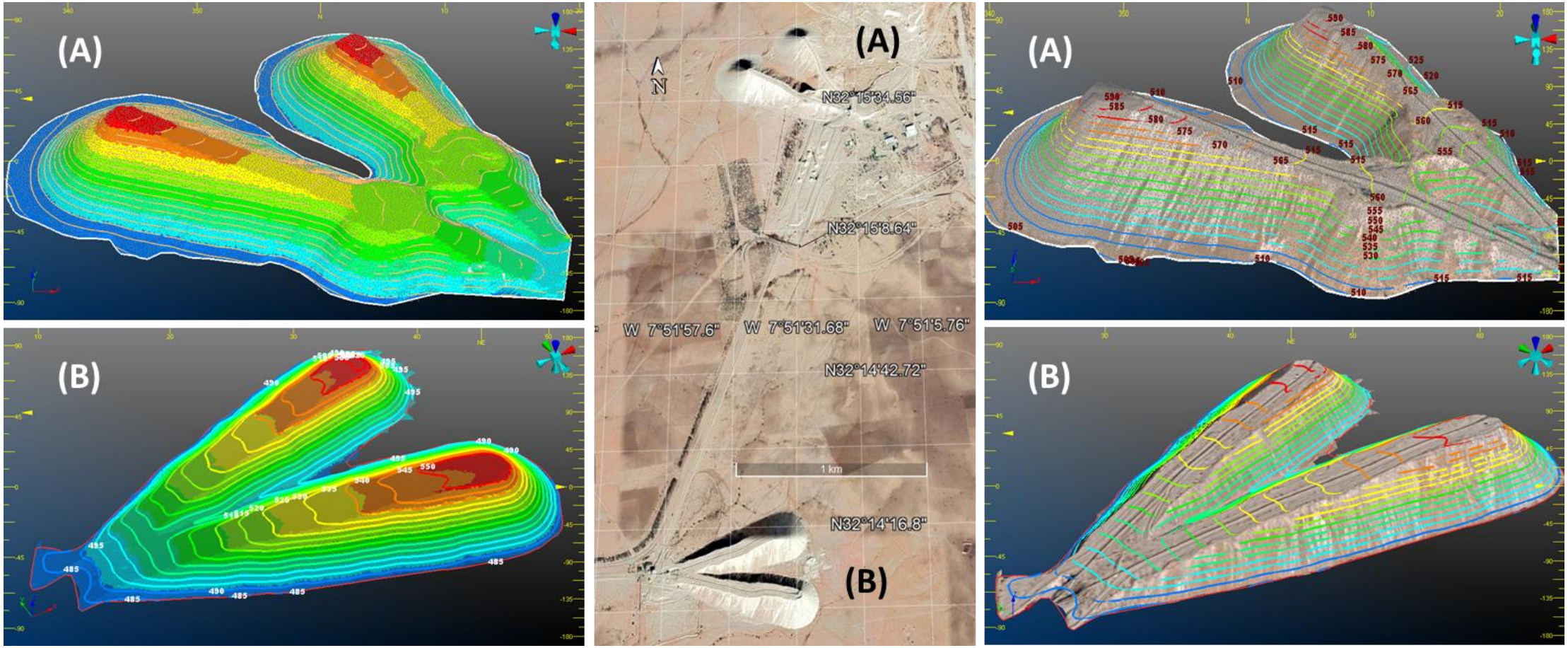
By-products generated by phosphate extraction

← Waste rocks & interlayers materials in Benguerir (16 x 13 km)

Phosphate sludge (18 x 19 km)

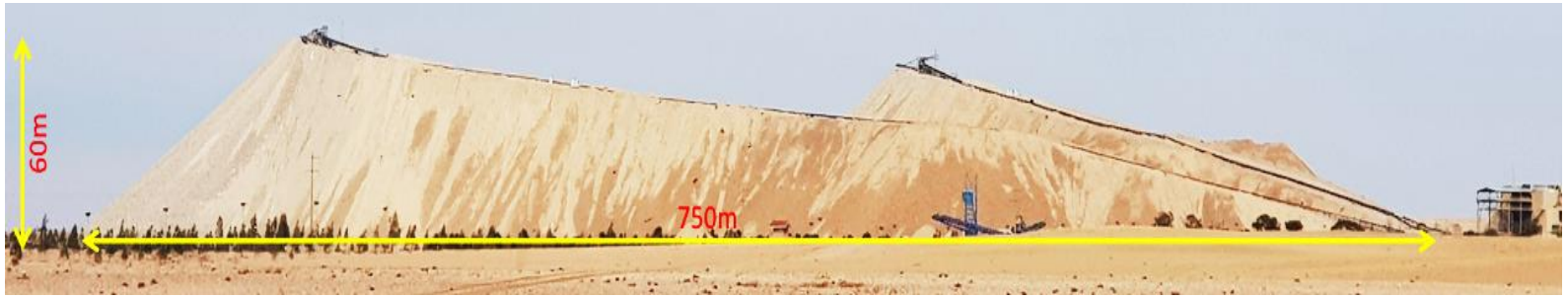
https://geemap.herokuapp.com/

PMWR from the open pit mine of Benguerir



3D models for destoning (A) and screening (B) PMWR piles

PMWR de Benguerir: Huge quantities

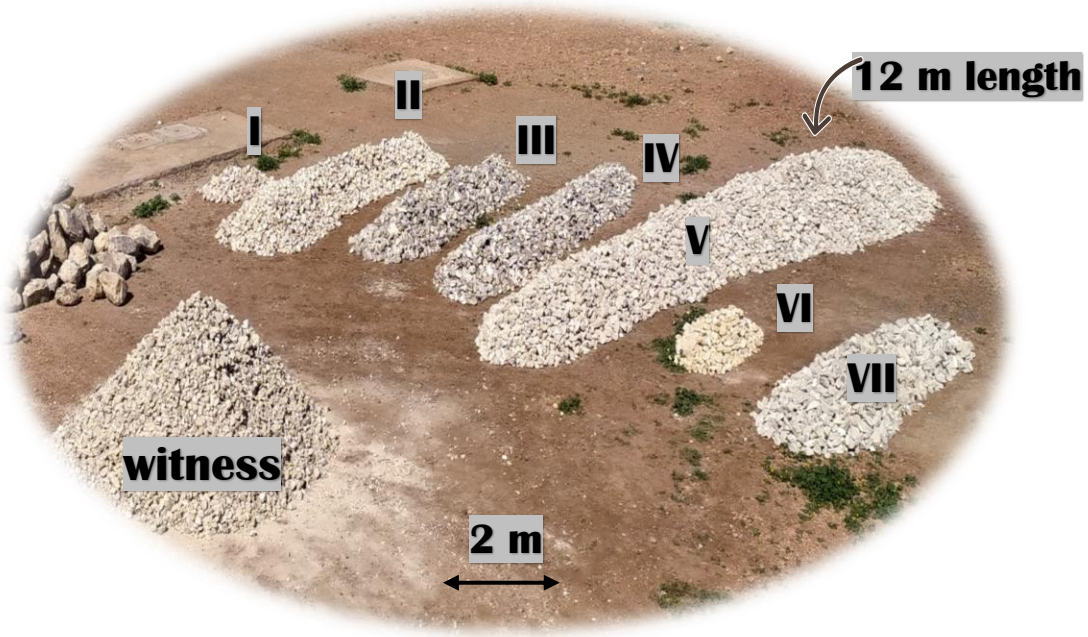


Destoning Spoil (particles of 90–150 mm) **7.43 Mm³ ~ 11.89 Mt**

These piles are characterized by high heterogeneity (large blocks to fine particles) & high segregation effect of the particles due to the disposition method.

Screening Spoil (particles of 30–90 mm) **7.67 Mm³ ~ 12.18 Mt**

Sampling & sorting: 25-tons of each stockpile




5%

I: Lightweight flintstone


20%

II: Silicious marls


14%

III: Phos-flint


14%

IV: Flintstone


30%

V: Indurated phosphate

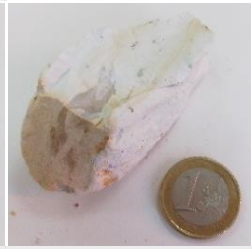

2%

VI: Tender marls


14%

VII: Dolomitic limestone

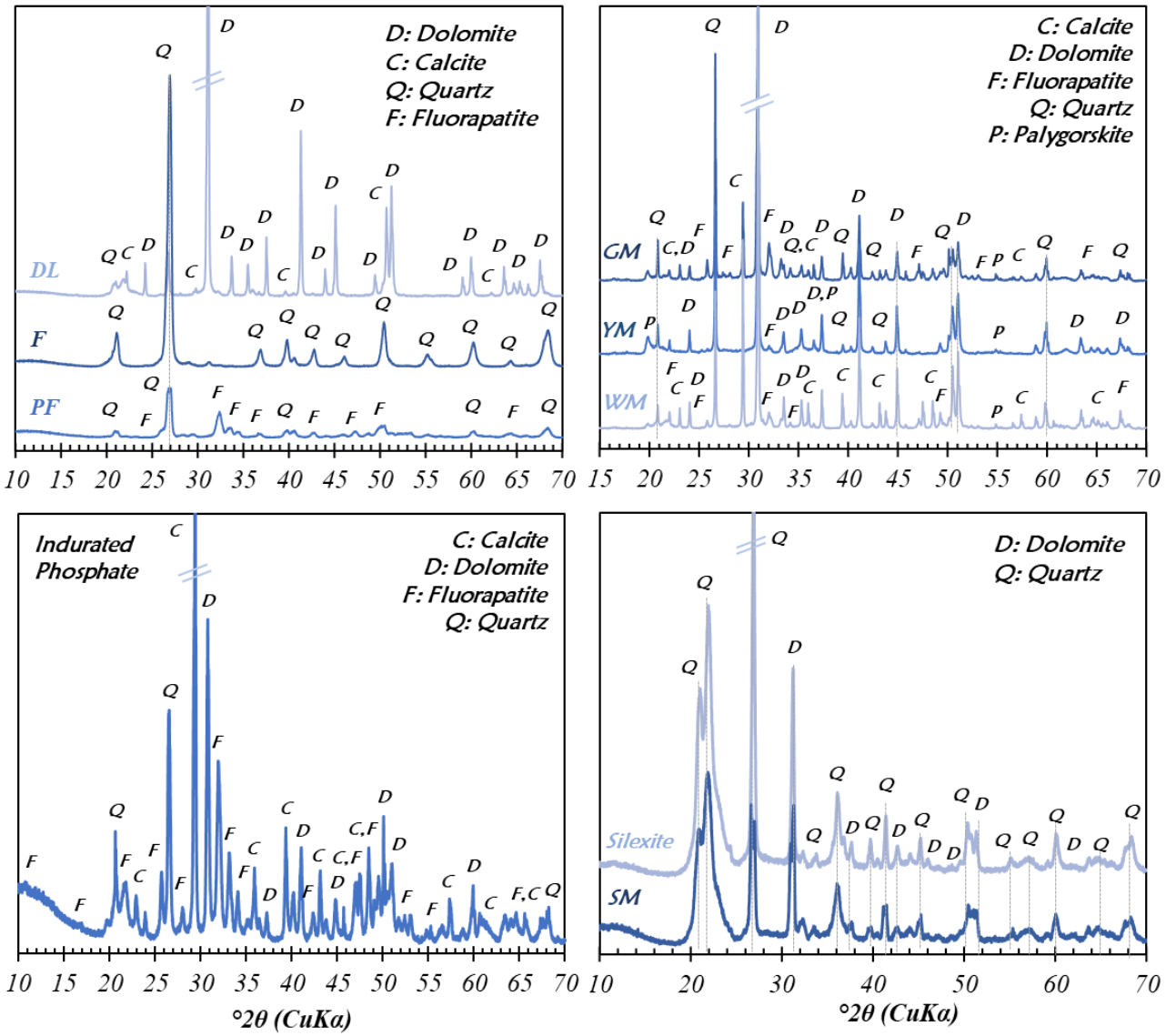
Petrographic macroscopic characterization

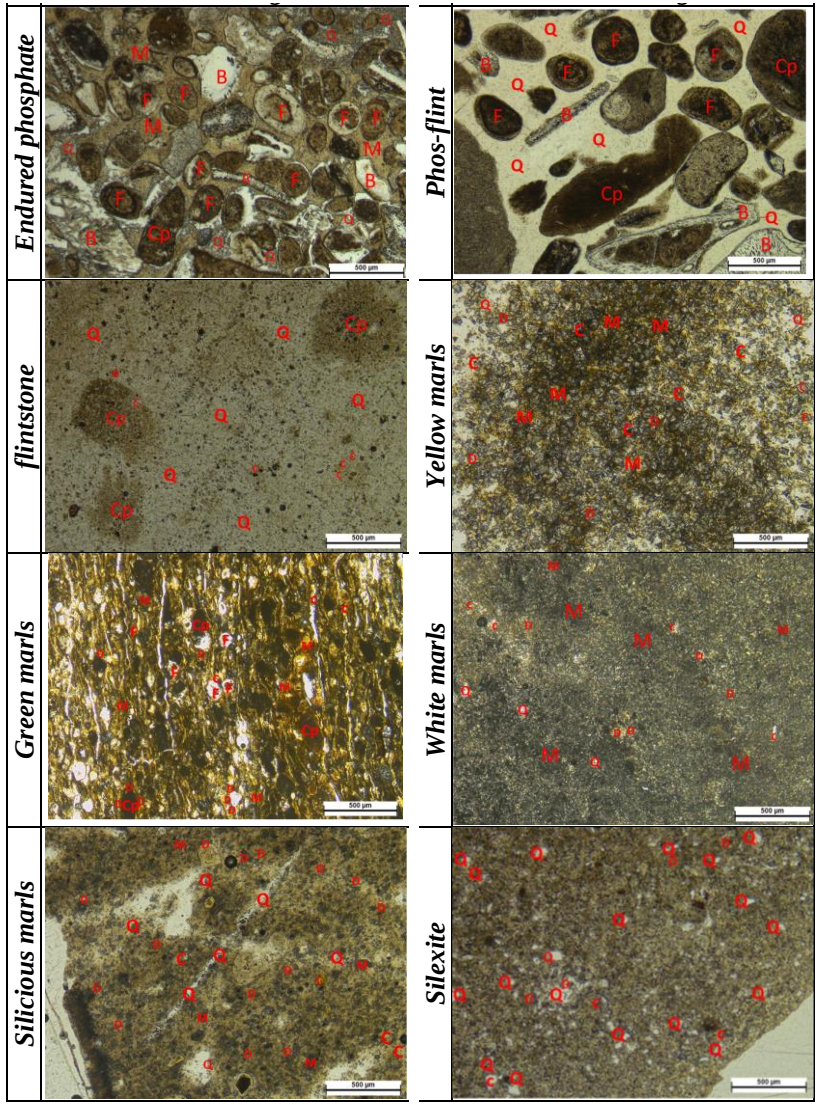
Lithology	Phosphate	Flintstones			Dolomitic limestone	Red clays	Marls	
		Flintstone	Phos-flint	Silexite			Silicious & calcareous	Tender
Picture								
General aspect	Fine/coarse grains & consolidated	Sharp angle ribs slicers	Sharp angle ribs slicers	Very light & sticky to the tongue	Very dense	Very tender & crumbly	Compact, lightweight, & sticky to the tongue	Tender
Surface texture	Granular welded	Crystalline	Packstone	Massive	Mudstone	Sprayed	Laminated to massive	
Break	Irregular	Conchoidal & irregular	irregular	irregular	Regular net	None	Irregular	Sprayed tender
Color	Greyish	Dense brown	Black + greyish elements	Purplish pink	Whitish beige	Brick red	Whitish & Whitish beige	Yellow, white, & green
Sparkle	No shine	Weak	Weak	No shine	Low	No shine	No shine	
Effervescence at HCL	Weak	Negative	Very weak	Very weak	Positive and strong	Very weak	Weak to moderate	
Density	+++	++++	++++	++	+++++	+	++	+
Hardness	+++	++++	++++	+++	++++	+	+++	+

Chemical & mineralogical properties

Lithologies	Tender marls			Dolomitic limestone	Siliceous marls	Flintstones			Phosphate rocks
	White	Yellow	Green			Flintstone	Silexite	Phos-flint	
Chemical composition, wt.%									
SiO_2	11.3	18.3	16.2	7.84	74.0	93.6	80.1	34.8	15.6
Al_2O_3	1.13	3.35	2.38	0.37	1.49	0.28	1.03	–	0.30
MgO	13.7	18.2	11.5	23.6	4.52	0.43	3.70	0.42	4.63
CaO	36.4	24.1	34.1	28.4	7.23	1.55	4.54	33.6	42.6
P_2O_5	2.35	0.99	7.89	0.98	1.88	1.85	0.70	25.0	23.6
Other	0.80	3.28	2.06	0.60	0.80	0.46	0.81	0.76	0.94
LOI	34.4	31.7	25.7	38.1	10.1	1.84	9.14	5.52	12.4
Mineralogical composition, %									
Palygorskite	38.6	47.9	49.1	–	–	–	–	–	–
Dolomite	35.9	33.5	15.8	67.7	48.8	1.94	37.6	3.91	30.4
Apatite	12.3	5.66	22.1	7.18	–	1.20	–	38.3	47.7
Calcite	10.4	8.2	10.7	16.5	–	1.78	–	10.3	13.0
Quartz	2.79	4.69	2.79	8.55	51.2	95.1	62.4	47.5	8.81

Mineralogical Characterization

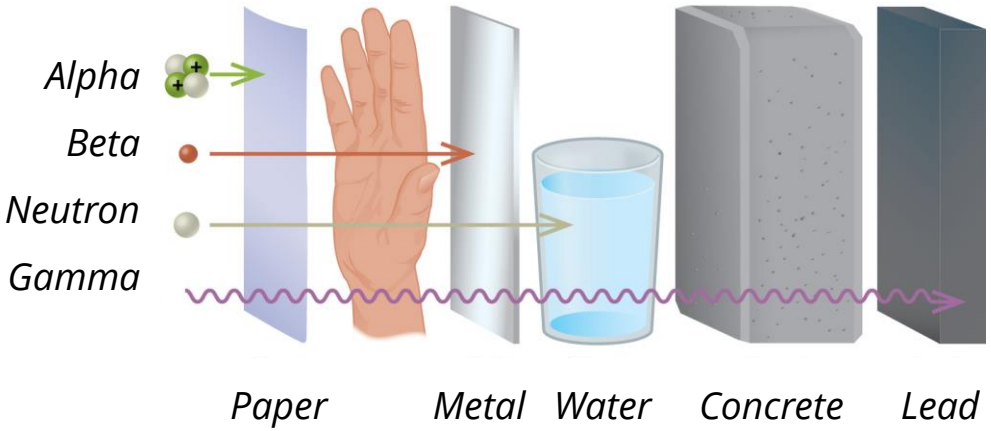




Gamma-ray radiation

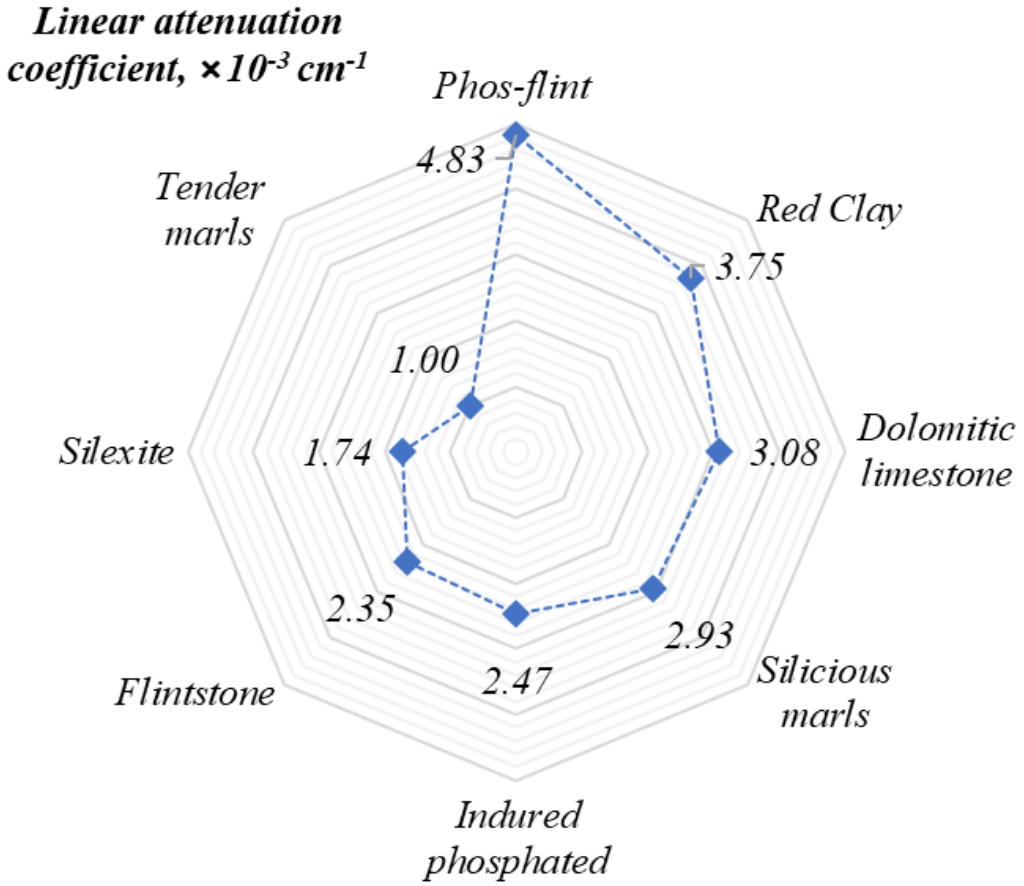
Gamma-ray:

- Very high penetrating power
- Very low ionizing power



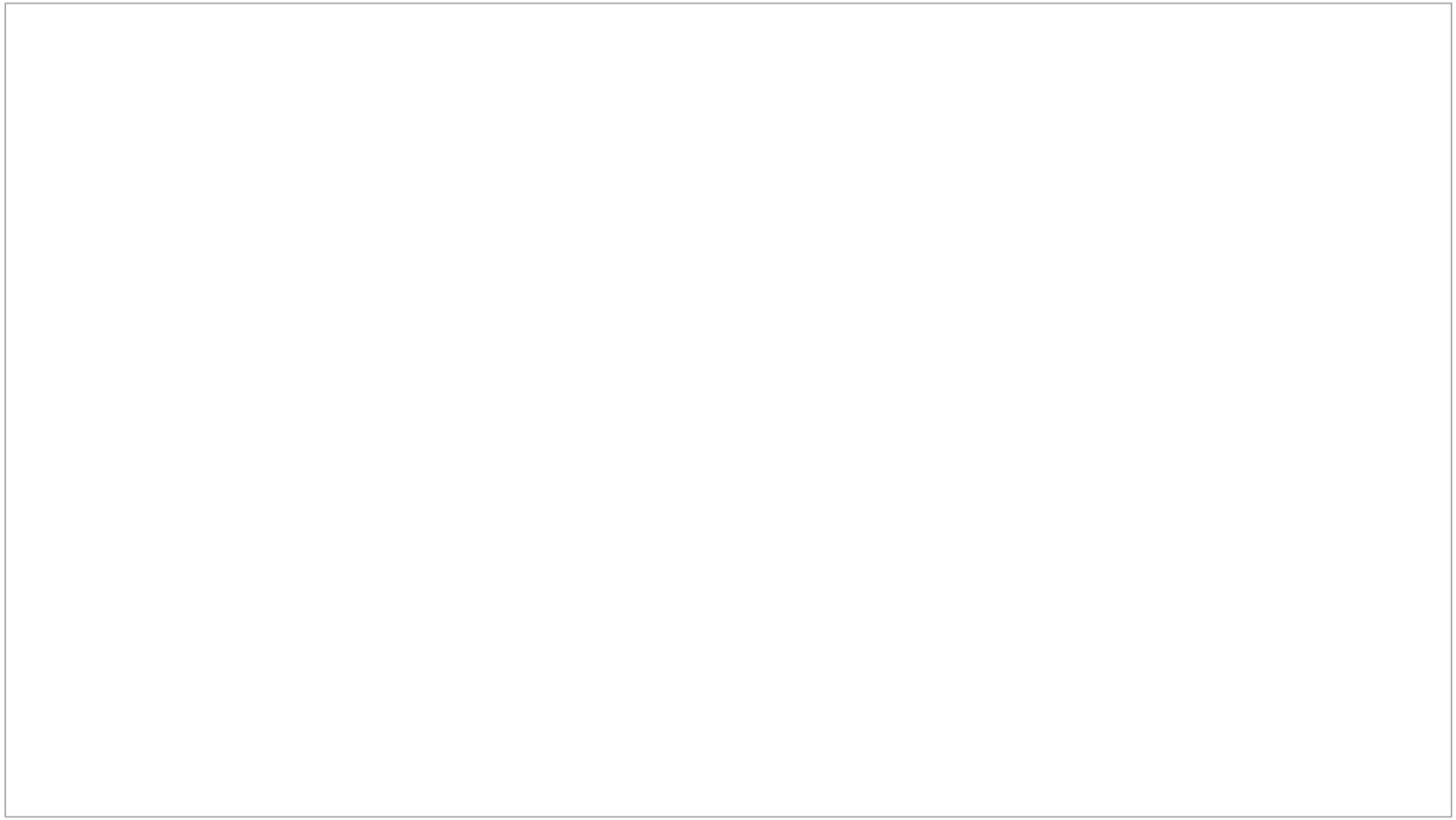
The ability of different types of radiation to pass through material is shown.

→ The use of phos-flint & dolomitic limestone as aggregate will enhance the concrete nuclear shielding

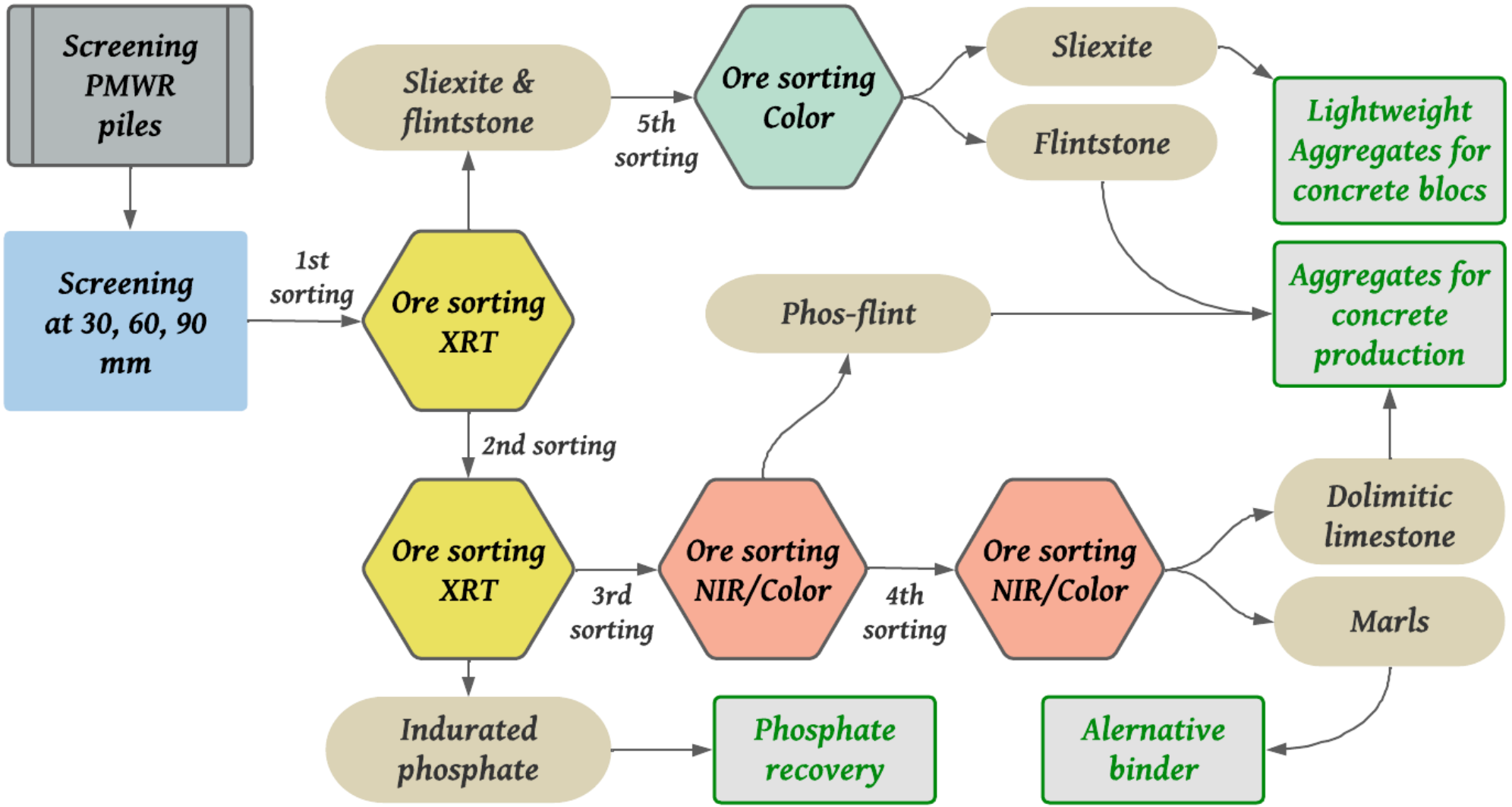


Calculated linear attenuation coefficient of the different lithologies

Based-sensors ore sorting technique

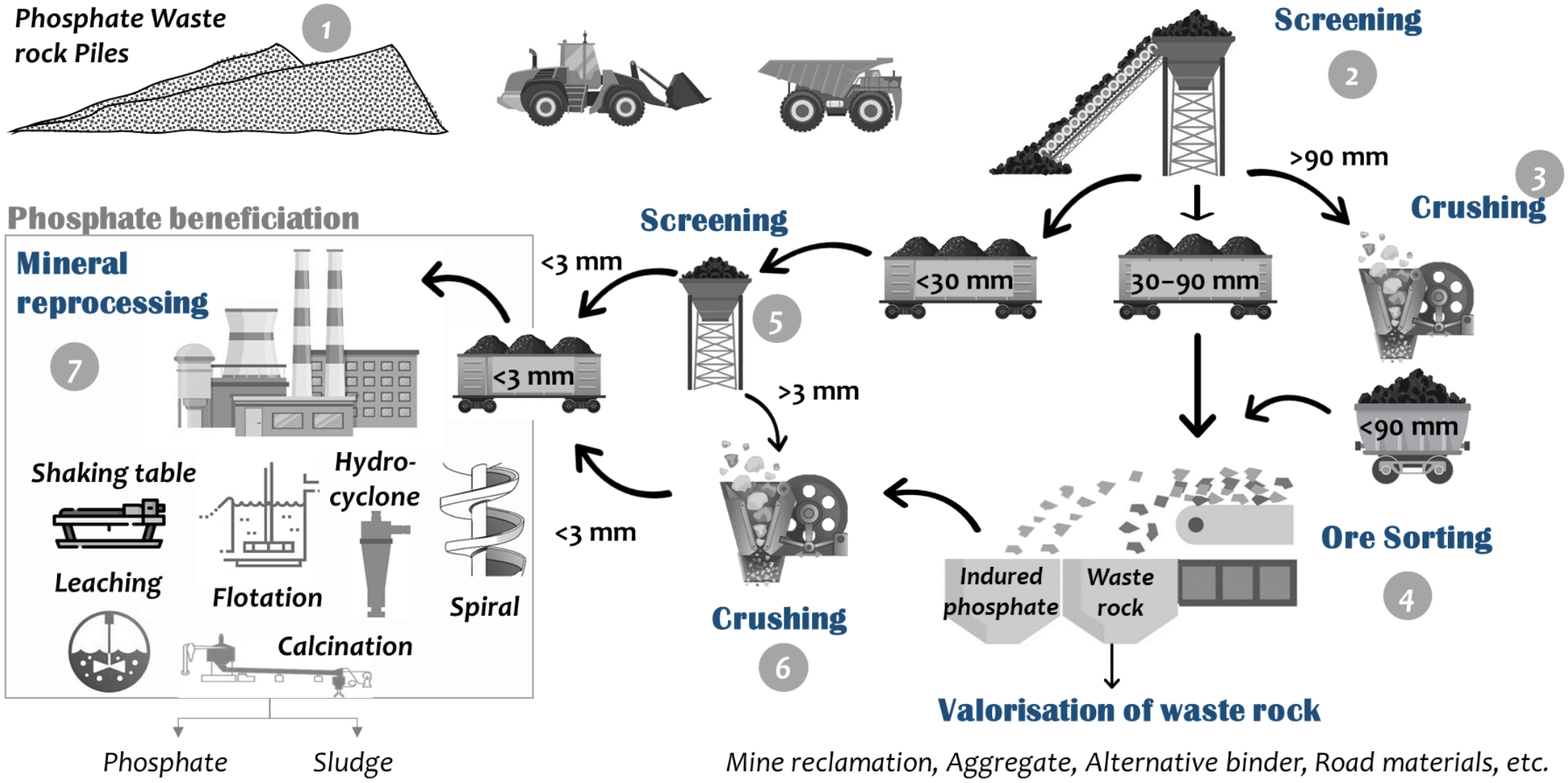


Proposed ore sorting strategy/Potential uses



Amar et al., 2023, under review

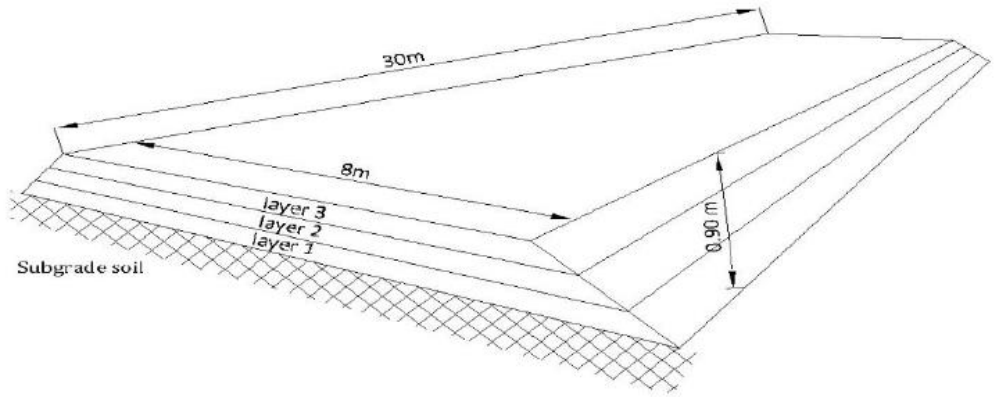
Potential uses: Phosphate recovery



Potential uses: Road construction

Valorization of PMWR as Materials for Road Construction: Work of Dr. Mustapha Amrani

Figures illustrating the field trial embankment construction



Physical and geotechnical properties of collected materials

Test		I1	I2	I3	I4	I5
Moisture Content	wt. %	3.4	3.7	3.6	2.9	3.1
Geotechnical properties—Natural parameters						
Proctor Test						
Optimum Moisture content (w_{opn})	wt. %	13.40	12.90	15.20	14.60	13.23
Maximum dry density $\gamma_{d\ max}$	kN/m^3	*	*	17.9	*	*
Shear test						
Friction angle (Ø′)	degrees	30.00	32.40	27.00	27.5	27.00
Cohesion (c′)	kPa	4	5	6	7	7
CBR	%	*	*	13	*	*
Atterberg limit						
Liquid limit	wt. %	39	37	41	44	45
Plastic limit	wt. %	26	25	26	29	30
Plasticity index	wt. %	13	12	14	15	15
Methylene blue value	g/100g	0.59	0.58	0.67	0.68	0.71
Carbonate content	wt. %	30	29	33	32	33
Geotechnical Properties–Mechanical behavior						
Specific (particle) densi	kN/m^3	2.61	2.65	2.56	2.6	2.58
Los Angeles abrasion test 25/50	wt. %	48	46	66	67	53
Mico Deval test 25/50	wt.%	55	50	68	70	54
Degradability coefficient	wt.%	10.10	9.10	13.80	14.60	12.70
Fragmentability coefficient	wt.%	8.90	7.50	10.10	11.40	10.50
Material classification	-	C_1B_5	C_1B_5	C_1B_5	C_1B_5	C_1B_5

* Proportion of particles greater than 20 mm exceeds 30% of the mass of the material, in this case, the maximum dry density of the proctor and the value of CBR test are not significant.

Amrani et al., 2019, Valorization of Phosphate Mine Waste Rocks as Materials for Road Construction. Minerals, 9, 237. DOI: 10.3390/min9040237

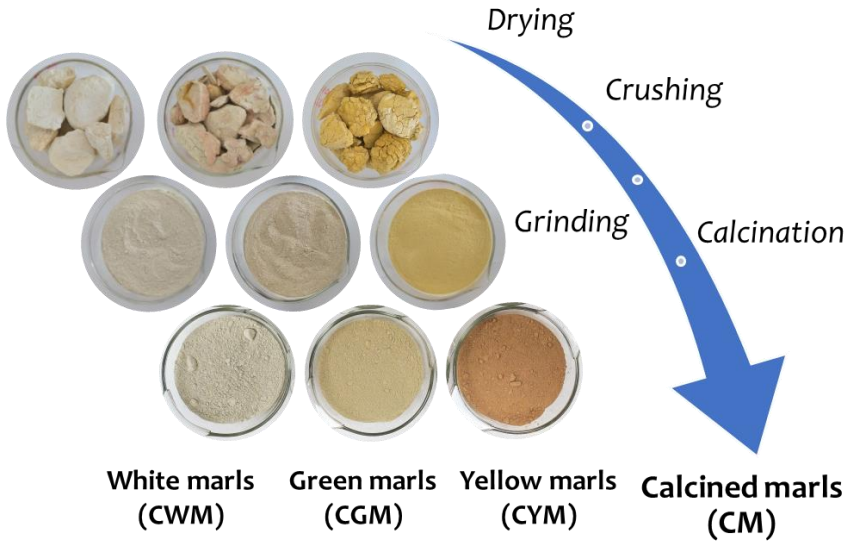
Potential uses: Road construction

Construction of experimental embankment and subgrade plots - full-scale tests

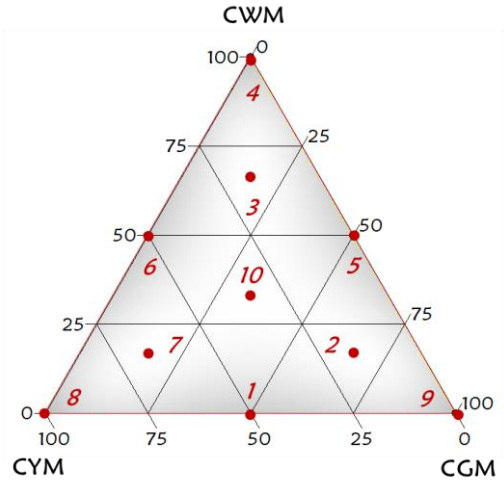
Two kind of waste rocks were tested with natural water content or with humidification

Amrani et al., 2019, Valorization of Phosphate Mine Waste Rocks as Materials for Road Construction. Minerals, 9, 237. DOI: 10.3390/min9040237

Potential uses: Tender marls as alternative binders

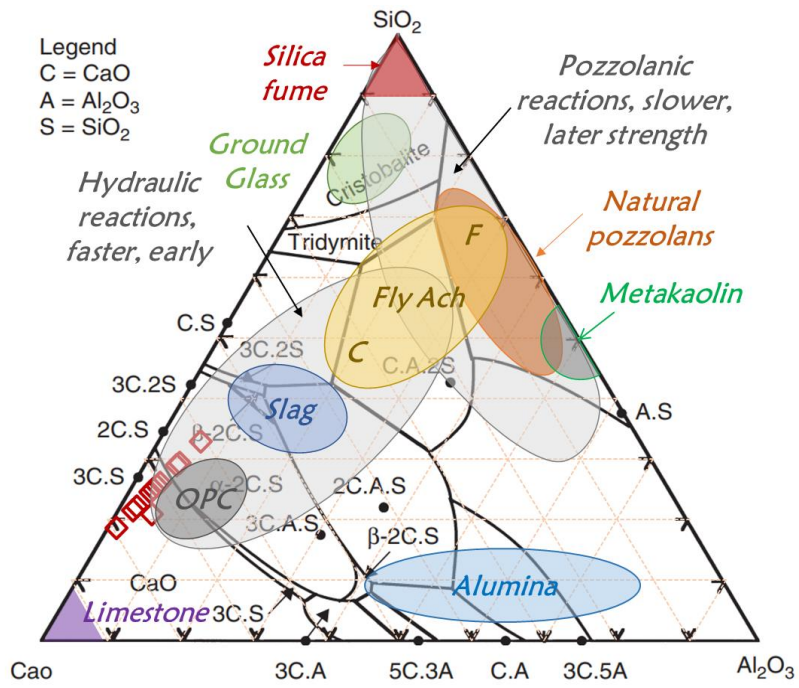


Treatment process of the marls



DoE: mixture of the 3 marls

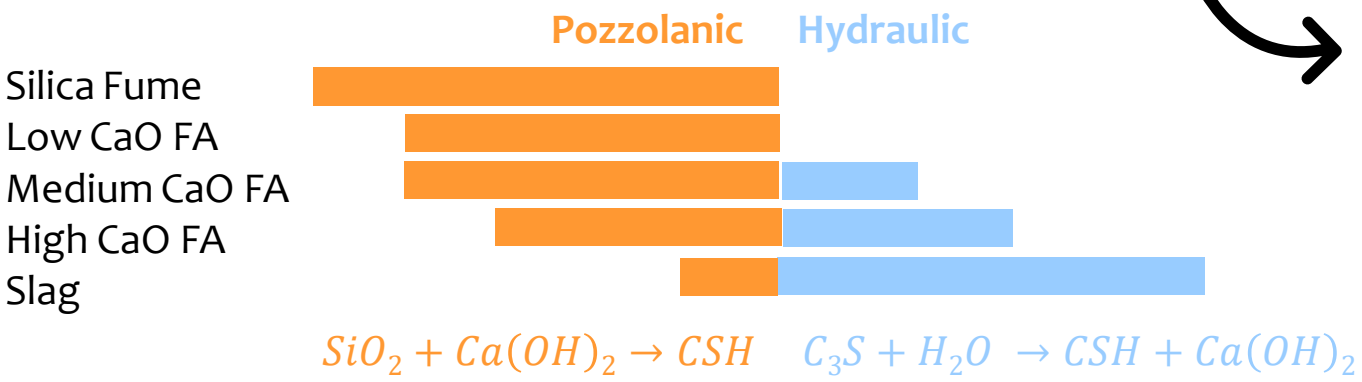
Natural Hydraulic lime
CEM:CM of 1:1



Ternary Keil-Rankin diagram

57–69% of carbonates (CaO+MgO)

18–40% of SiO_2+Al_2O_3+Fe_2O_3



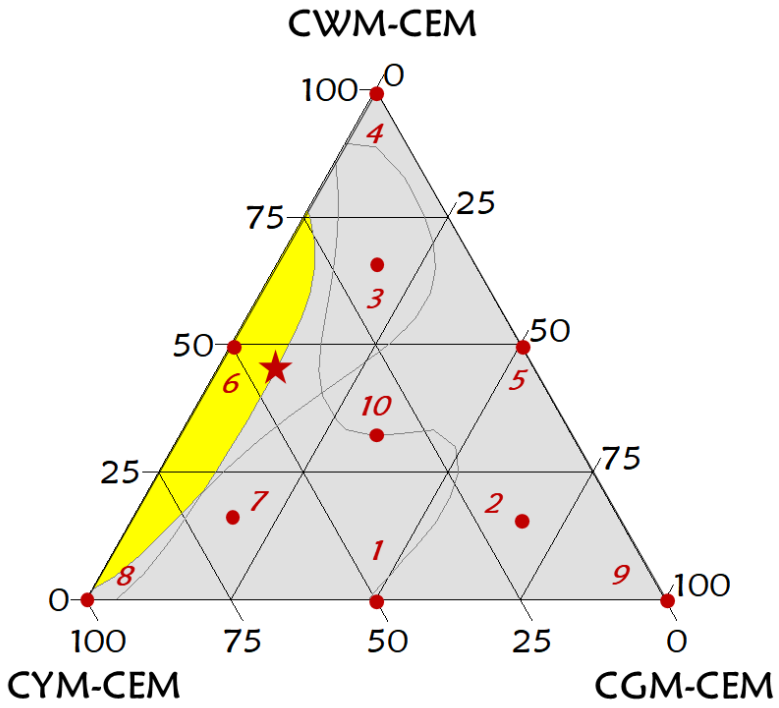
$SiO_2 + Ca(OH)_2 \rightarrow CSH$ $C_3S + H_2O \rightarrow CSH + Ca(OH)_2$

Safhi et al., 2022, Elaboration of a blended binder based on marls from phosphate mines waste rocks, CBM, 347(2):128539. DOI: 10.1016/j.conbuildmat.2022.128539

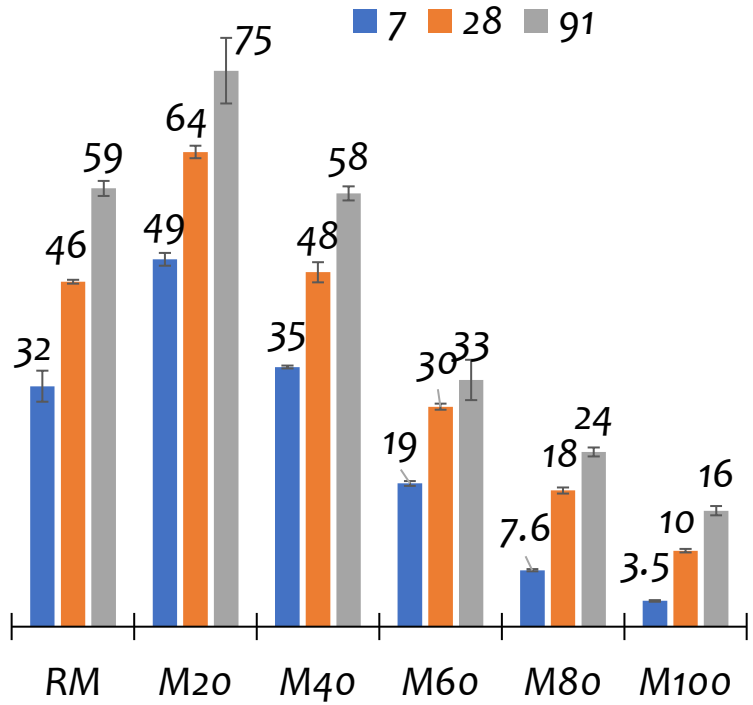
Potential uses: Tender marls as alternative binders

What was already done!

- **Detailed characterization:** physio-chemical & mineralogical properties, TGA analysis.
- **Optimization of the mixture:** Setting times, hydration kinetics, & compressive strengths.
- Varying the **incorporation rate** of calcined marls in the blended binder.
- **Perspectives:** testing CM as repairing binder for historical buildings & as hydraulic road binder.



Optimization criteria: 75% of reference strength at different curing age



Compressive strength of the cement-marl systems at different curing age

Safhi et al., 2022, Elaboration of a blended binder based on marls from phosphate mines waste rocks, CBM, 347(2):128539. DOI: 10.1016/j.conbuildmat.2022.128539

Potential uses: PMWR for aggregate production

Physio-mechanical characterization of the potential rocks

Reserve of hard rocks (~20–30% of total piles) equal to ~4 Mm³

Phos-flint

Flintstone

Dolomitic limestone

Rock type/Properties		Flint	Phos- flint	Dolomitic Limestone
Absolute gravity, t/m³		2.61	2.76	2.87
UCS, MPa	Cubes	–	208 ± 27	167 ± 48
	Cylinder	–	70	>120
Hardness, Mohs scale		7	$6^{1/2}$	6

Potential uses: PMWR for aggregate production

Characterization of aggregates compared to different specifications

The three rocks were crushed using a laboratory jaw crusher to produce concrete coarse aggregates respecting the n° 7 mesh of ASTM C33 (2018) standard. The physio-mechanical properties of the produced aggregates were tested.

Property	*Standard*	*Values range*	*Flintstone*	*Phos-flint*	*Dolomitic limestone*
Specific density, t/m³	ASTM C33	2.30–2.90	2.59	2.59	2.60
	ACI 211.1	2.50–3.00			
	NF EN 12620	2.00–3.00			
Water Absorption, %	ASTM C33	0.50–4.00	1.7	2.7	2.9
	ACI 211.1	0.20–4.00			
Bulk density, t/m³	ASTM C33	1.28–1.92	1.30	1.30	1.43
Water content, %	ASTM C33	0.00–2.00	0.50	0.80	0.30
Los Angeles value, %	ACI 211.1	25.0–50.0	21.0	30.0	26.0
(NF EN 1097-2)	NF EN 12620	–	(21%) LA_{25}	(30%) LA_{30}	(26%) LA_{30}
Micro-Deval value, % ***(NF EN 1097-1)***	NF EN 12620	–	(5%) MDE_{10}	(9%) MDE_{10}	(15%) MDE_{15}
Flakiness index, % ***(NF EN 933-3)***	NF EN 12620	–	(32%) FI_{35}	(26%) FI_{35}	(23%) FI_{35}

→ The three aggregates conform to the specifications to be use as coarse aggregates, and they seem adequate candidates to produce ordinary concrete.

Potential uses of lightweight aggregate

Silexite and silicious marls found to have similar properties including the low density and could be used as lightweight aggregate (LWA) for lightweight concrete production.

Physical properties of the silexite from PMWR compared to previous studies

Properties	Silexite				
	From PMWR		Sidibé, 1995	Cisse et al., 1999	BA, 2008
Granular fraction	0/5 mm	5/12[5] mm	0/31[5] mm	0/3 mm	0/40 mm
Los Angeles, %	–	28.0	9	–	21
Micro Deval, %	–	–	21.4	–	17
Flakiness coefficient, %	–	32.8	–	–	24.9
Specific density	2.48		2.63	2.73	2.40
Apparent density	1.68	1.73	1.56	–	–
Absorption, %	17.4	16.5	–	1.47	–
Porosity, %	–	–	–	–	15.6
Proctor – W_{OPT}, %	–		–	6	9.5
Proctor – γ_{dmax}, t/m³	–		–	1.94	2.40

The thermal properties of four samples of silexite (about 82×42×10 mm) were tested. The findings result in an average ***thermal conductivity*** of ***0.894 ±0.113 W/m.K*** and an average ***thermal diffusivity*** of ***0.153 ±0.039 mm²/s***.

Potential uses of lightweight aggregate

Concrete blocks based on silexite, silicious marls, and calcined marls

Nine cylindrical specimens of 75Ø150 mm were prepared			
Mortar mix proportion by mass	*Calcined marls*		1
	Fine aggregate silexite		3
	w/b		0.8
	Sand absorption, %		17.4
Hardened properties (average of 3 tests)	*UCS, MPa*	*7-d*	1.04 ±0.06
		28-d	3.09 ±0.43
		90-d	4.94 ±0.56
	Apparent volumetric mass, kg/m³		1684 ±48

Visual aspect of the fine aggregates

Visual aspect of the prepared specimen

→ Despite the achieved low compressive strength, this preliminary study showed that achieving lightweight concrete blocks using the LWA from PMWR is possible.

Conclusions and perspectives

This research characterized the PMWR of Benguerir mine site & suggested several recovery pathways for those materials. The following conclusions could be drawn:

1. ***Phosphate recovery:*** The PMWR contain ~45–50% of coarse material (>30 mm) that can be separated by screening for ore sorting. The recovered indured phosphate constituting ~25% of the PMWR can be valorized by joining the conventional mineral processing with the fine fraction (<30 mm).
2. ***Road construction materials:*** Valorization of the PMWR as construction road material was already tested & proved for the sub-layer foundation. However, after recovery of the indured phosphate by ore sorting alongside with flint, phos-flint, and dolomitic limestone, the rest of this process will lead to a new disposal.
3. ***Concrete aggregates:*** Flint, phos-flint, and dolomitic limestone have good properties to be used as aggregates. However, these lithologies could present several difficulties in terms of deleterious substances presence, the chemical stability, and the shape for use as concrete aggregates. This should be investigated.
4. ***Alternative binders:*** The tender marls have an interesting hydraulicity and medium pozzolanicity reaction that qualifies them to be used as alternative binder. Previous studies revealed that upcycling tender marls as alternative binder would have a great ecological impact by reducing the CO_2 footprint.
5. ***Lightweight aggregate:*** The silexite & silicious marls have a considerable lightweight density to be used to produce lightweight concrete blocks. The preliminary mix design with calcined marls & the thermal conductivity properties confirmed such a feasibility.

→ Valorization of those by-products would have a great environmental impact on the urban planning.

Global impact of the project

Alternative materials Cleaner technologies Sustainable infrastructure	9 INDUSTRY, INNOVATION AND INFRASTRUCTURE	11 SUSTAINABLE CITIES AND COMMUNITIES	Build with local materials Affordable products (with low cost)
Sustainable & efficient management of natural resources	12 RESPONSIBLE CONSUMPTION AND PRODUCTION	13 CLIMATE ACTION	Reduction of CO_2 emissions Reduce the need for mining

Publications

Contents lists available at ScienceDirect

Materials Today: Proceedings

journal homepage: www.elsevier.com/locate/matpr

Calcined marls as compound of binary binder system: Preliminary study

Amine el Mahdi Safhi [a,*], Yassine El Khesssaimi [a], Yassine Taha [a], Rachid Hakkou [a,b], Mostafa Benzaazoua [a]

Contents lists available at ScienceDirect

Construction and Building Materials

journal homepage: www.elsevier.com/locate/conbuildmat

Elaboration of a blended binder based on marls from phosphate mines waste

Amine el Mahdi Safhi [a,*], Yassine Taha [a], Mustapha El Ghorfi [a,b], Rachid Hakkou [a,b], Mostafa Benzaazoua [a]

Contents lists available at ScienceDirect

Journal of Cleaner Production

journal homepage: www.elsevier.com/locate/jclepro

Characterizations and potential recovery pathways of phosphate mines waste rocks

Amine el Mahdi Safhi [a,*], Hicham Amar [a], Yahya El Berdai [a], Mustapha El Ghorfi [a,b], Yassine Taha [a], Rachid Hakkou [a,b], Muthanna Al-Dahhan [c], Mostafa Benzaazoua [a]

Contents lists available at ScienceDirect

Materials Today: Proceedings

journal homepage: www.elsevier.com/locate/matpr

Synthesis of MgO-Belite calcium sulfoaluminate cement from phosphate mine waste rock and phosphogypsum

Yassine El Khessaimi *, Yassine Taha, Amine El Mahdi Safhi, Rachid Hakkou, Mostafa Benzaazoua


المملكة المغربية
وزارة التجهيز والماء
MINISTÈRE DE L'ÉQUIPEMENT ET DE L'EAU
الجمعية المغربية الدائمة
لمؤتمرات الطرق
L'Association Marocaine
Permanente des Congrès de la Route
تحت الرعاية السامية لصاحب الجلالة الملك محمد السادس نصره الله
SOUS LE HAUT PATRONAGE DE SA MAJESTÉ LE ROI MOHAMMED VI
11ème
المؤتمر الوطني للطرق
Congrès National de la Route
MERCI
تحت شعار
أية مكانة لتطوير البنية التحتية الطرقية في تنزيل النموذج الجديد للتنمية الإقتصادية و الإجتماعية بالمغرب ؟
SOUS LE THÈME
Quels rôles de l'infrastructure routière dans le nouveau modèle de développement économique et social du Maroc ?
10/12 NOV نونبر
DAKHLA 2022
الداخلة
DAKHLA