

See discussions, stats, and author profiles for this publication at:
<https://www.researchgate.net/publication/236022028>

Utilization of Jarosite/Alunite residue for mortars restoration production

Article in *Matériaux et Constructions* · January 2010

DOI: 10.1617/s11527-009-9478-y

CITATIONS

11

READS

44

7 authors, including:



[Eleni Aggelakopoulou](#)

Acropolis Conservation Service, Greek...

29 PUBLICATIONS 393 CITATIONS

[SEE PROFILE](#)



[Petros E Tsakiridis](#)

National Technical University of Athens

66 PUBLICATIONS 1,228 CITATIONS

[SEE PROFILE](#)



[Styliani Agatzini -Leonardou](#)

National Technical University of Athens

33 PUBLICATIONS 665 CITATIONS

[SEE PROFILE](#)

All content following this page was uploaded by [Petros E Tsakiridis](#) on 27 November 2016.

The user has requested enhancement of the downloaded file. All in-text references [underlined in blue](#) are linked to publications on ResearchGate, letting you access and read them immediately.

Utilization of jarosite/alunite residue for mortars restoration production

M. Katsioti · O. Mauridou · A. Moropoulou ·
E. Aggelakopoulou · P. E. Tsakiridis ·
S. Agatzini-Leonardou · P. Oustadakis

Received: 9 April 2008 / Accepted: 29 January 2009 / Published online: 3 February 2009
© RILEM 2009

Abstract The present study was carried out to produce artificial hydraulic lime mortars for repair and conservation of historic masonry using a jarosite/alunite precipitate, a waste product of a novel Greek hydrometallurgical process developed to treat economically low grade nickel oxides ores. Alternative mortars were prepared by mixing lime powder, quartz sand and the above residue, substituting lime up to 50%. The mortars were prepared and tested according to European Norm EN 1015. They were cured for periods of 28 and 90 days and the compressive and flexural strengths were determined. The best mechanical behavior was observed for the mortar with 50% lime replacement, which also presented a low ratio of compressive to flexural strength (f_c/f_f). X-Ray diffraction, TG-DTA and mercury porosimetry were

used to characterize the hydration products at 28 and 90 days. The results showed that the jarosite/alunite residue was dissolved in the high alkaline environment of the mortar, producing $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ and AlOOH . During hydration, gypsum and some of the $\text{Ca}(\text{OH})_2$ were consumed, together with aluminum hydroxide in order to produce ettringite, a fact that improved the mechanical behavior of the produced mortars.

Keywords Restoration mortars · Lime · Jarosite/alunite residue · Mechanical strength · Characterization

1 Introduction

Historic buildings need special care to preserve their special character. Building methods today are often different to those used in the past and modern practices are not necessarily the best practices when applied to historic buildings. This grant is given partly in recognition of the fact that sensitive restoration often costs more than standard modern practices.

Lime used to be traditional binder, used for a large variety of mortars for brickwork, stonework, renders and plasters in the ancient buildings of Europe [1]. But for restoration purposes usually current materials and techniques are employed. These are often found

M. Katsioti · O. Mauridou
Section of Chemical Sciences, School of Chemical
Engineering, National Technical University of Athens,
Athens, Greece

A. Moropoulou · E. Aggelakopoulou
Section of Materials Science and Engineering, School of
Chemical Engineering, National Technical University of
Athens, Athens, Greece

P. E. Tsakiridis (✉) · S. Agatzini-Leonardou ·
P. Oustadakis
Section of Metallurgy and Materials Technology, School
of Mining and Metallurgical Engineering, National
Technical University of Athens, Athens, Greece
e-mail: ptsakiri@central.ntua.gr



to be ineffective and can cause damage. Lime-based mortars were commonly used in building until the second half of the nineteenth century, when they started to be replaced by a new binder, namely Portland cement. The historic buildings should be properly looked after and only the highest standards of current conservation practice are acceptable for works to ancient buildings.

The application of cement mortars in the restoration of historic buildings has had numerous adverse effects because the cement-based mixes are too hard, rigid, and impermeable. In general, mortars should be more permeable to vapor transport than the other masonry materials used so that water, which contains damaging ions, can evaporate before it spreads throughout the structure [2, 3]. The usual problems encountered during restoration of a historical masonry with strong adhesion mortars, are the irreversibility of the method, the incompatibility between the old and new mortar and the lowering of the masonry porosity, resulting in the increase of humidity [4, 5].

Cement-based mortars show a high content of soluble salts, potentially dangerous for decay of ancient mortar by crystallization and/or hydration (cycles) [6]. Also, cement-based mortars are less permeable than lime mortars, retaining an excess water, which initiate alteration phenomena. Finally, cement-based mortars exhibit a high compressive strength, but far from being favorable, this is a source of problems [7, 8].

Modern mortars and adhesives are generally less porous than natural stones and bricks, and they have a mechanical resistance and a thermal expansion coefficient higher than those of the materials to which the mortars themselves are applied. When evaporation, thermal and mechanical stresses are present, and the possibility of salt crystallization exists, the introduction in the masonry of hard, less porous materials can be very dangerous. Stresses are concentrated on the surrounding ancient, weaker material which starts deteriorating in turn. For these reasons the use of mortars with characteristics as similar as possible to those of the materials to be repaired, is recommended [9].

The use of materials similar to the original ones in a restoration process is an oft repeated recommendation of many researchers. Some previous works have insisted upon the compatibility between the new

repair mortar and the original components of the masonry [10, 11]. Repair mortar which is too strong restrains movement and leads to stress that can cause failure in the original masonry [12]. In several recent cases, extensive damage to the ancient masonry due to incompatibility of the cement-based mortars with the old materials has been clearly established [13].

An ideal mortar for restoration should present the following properties [9]:

- easy workability
- rapid and reliable setting in both dry and wet environments
- slow shrinking during setting
- mechanical and thermal characteristics, and porosity, similar to those of the components (natural stones, bricks, etc.) of the masonry
- soluble salts content as low as possible.

Any renovations to structures built with a lime-sand mortar should be completed with a similar lime-sand mix. The lime mortars are cleaner to work with, as a result of being plastic and more workable, and their appearance and color blend harmoniously with a mortar of the same composition. In contrast, common cement-based mortars produce a grisly result on older structures. However, the traditional lime/sand mortars, extensively used in ancient masonry in Europe, can sometimes give unsatisfactory results because of their difficult workability, their slow and poor setting in humid environments, and their incomplete carbonation beneath the surface.

The aim of the present research work was to investigate the possibility of using a hydrometallurgical residue, jarosite/alunite precipitate, for the production of lime restoration mortars. The jarosite/alunite group of isostructural minerals is described by the general formula $M(\text{Fe}_x\text{Al}_y\text{Cr}_z)(\text{SO}_4)_2(\text{OH})_6$, in which “M” may be Na^+ , K^+ , NH_4^+ or H_3O^+ and $x + y + z = 3$. For $x = 3$, the formula represents jarosite, whereas for $y = 3$ it represents alunite. The above precipitate is a byproduct of a new integrated hydrometallurgical method, developed by the Laboratory of Metallurgy of the National Technical University of Athens suitable to treat, efficiently and economically, the low-grade nickel oxide ores. It involves heap leaching of the ore by dilute sulphuric acid at ambient temperature, purification of the leaching liquors and recovery of nickel and cobalt. Iron, aluminum and chromium are then precipitated



as crystalline, easily filterable salts of the jarosite/alunite type, at atmospheric pressure [14–16].

The application of the Toxicity Characteristic Leaching Procedure (TCLP) test [17] has shown the jarosite/alunite precipitate to be environmentally stable and safe to be rejected in a tailings pond. It should also be noted that this precipitate, coming from the treatment of nickel oxide ores, does not contain hazardous elements such as Cd, As or Hg, by contrast with the jarosite precipitate produced during the hydrometallurgical extraction of zinc from sulfide ores. However, it is important to find use for this jarosite/alunite precipitate in order to reduce the cost of the hydrometallurgical process by avoiding the construction of a large landfill.

Three different mixtures were produced by substituting lime (powder) from 0% to 50% with the above precipitate. Lime powder was used as binder due to the higher and quasi-stable percentage of $\text{Ca}(\text{OH})_2$ content [18]. All mixtures were tested for, water demand, water retentivity, flow value, air content, density, compressive and flexural strength, in order to determine optimum percentage of substitution. In addition, XRD, TGA and mercury porosimetry were applied in order to study the hydration products, the hydration rate and the microstructure of the produced mortars.

2 Experimental

The chemical composition of the jarosite-alunite precipitate was carried out by atomic absorption spectrophotometer (Perkin Elmer 4000) and is listed in Table 1. The soluble salts content was determined by electrical conductivity measurements. Approximately 1 g of dried and powdered mortar sample was mixed with a known volume of distilled water. The total soluble salt content was determined by the electrical conductivity measurements of the salt extract solutions [19]. The mineralogical phases of the above precipitate, which were determined by XRD analysis, using a Siemens D5000 diffractometer with nickel-filtered $\text{CuK}\alpha_1$ radiation ($\lambda = 1.5405 \text{ \AA}$, 40 kV and 30 mA), are given in Fig. 1.

The particle size distribution of the jarosite/alunite residue, which was measured by a Cilas-Model 1064 laser diffraction particle size distribution analyzer, is given in Fig. 2. This was carried out using 0.1 g of

Table 1 Chemical analysis of jarosite/alunite mixed precipitate

Oxides	Content (%)
SiO_2	1.20
Al_2O_3	16.85
Fe_2O_3	39.66
Cr_2O_3	1.36
MgO	0.46
NiO	0.95
CoO	0.05
MnO	0.04
SO_3	18.86
Water soluble SO_3	14.60
Total soluble salts	1.21
LOI	19.92

powder in 100 cm^3 of ethanol, dispersed using an ultrasonic dispersion unit for 60 s. It was found that 50% of the mixed precipitate was below $8 \mu\text{m}$, whereas 100% of the material was below $50 \mu\text{m}$. The mean diameter of the precipitate was computed at $12.9 \mu\text{m}$.

Lime mortar containing only lime powder, as a binder, was compared with two other mixes in which lime was partially replaced by jarosite/alunite precipitate. The aggregate used was quartz sand of high purity, in accordance with the standard EN 196-1 [20]. Table 2 shows the percentages of the components employed for manufacturing mortars.

The mortars were prepared in accordance with the standard EN 1015 [21]. The mortar pastes were obtained using the amount of water required to achieve normal consistency (mortars with about the same consistency: 15.5–17.0 cm) and a good workability (measured by the flow table test) [22].

Aggregate and lime were blended for 5 min. Water was then added and mixed for 5 min at low speed, and finally for 1 min at high speed. The mortars were cast in prismatic $40 \times 40 \times 160 \text{ mm}$ moulds [23] and demoulded 72 h later. The pastes were slightly compacted [20] to remove air bubbles and voids. Curing was carried out at ambient laboratory conditions until the test day (RH $60 \pm 10\%$ and $20 \pm 2^\circ\text{C}$). Compressive strength measurements were conducted at the ages of 28 and 90 days on mortar prisms. For each mortar three prisms were cast, which means three specimens for flexural test and six specimens for compressive test.

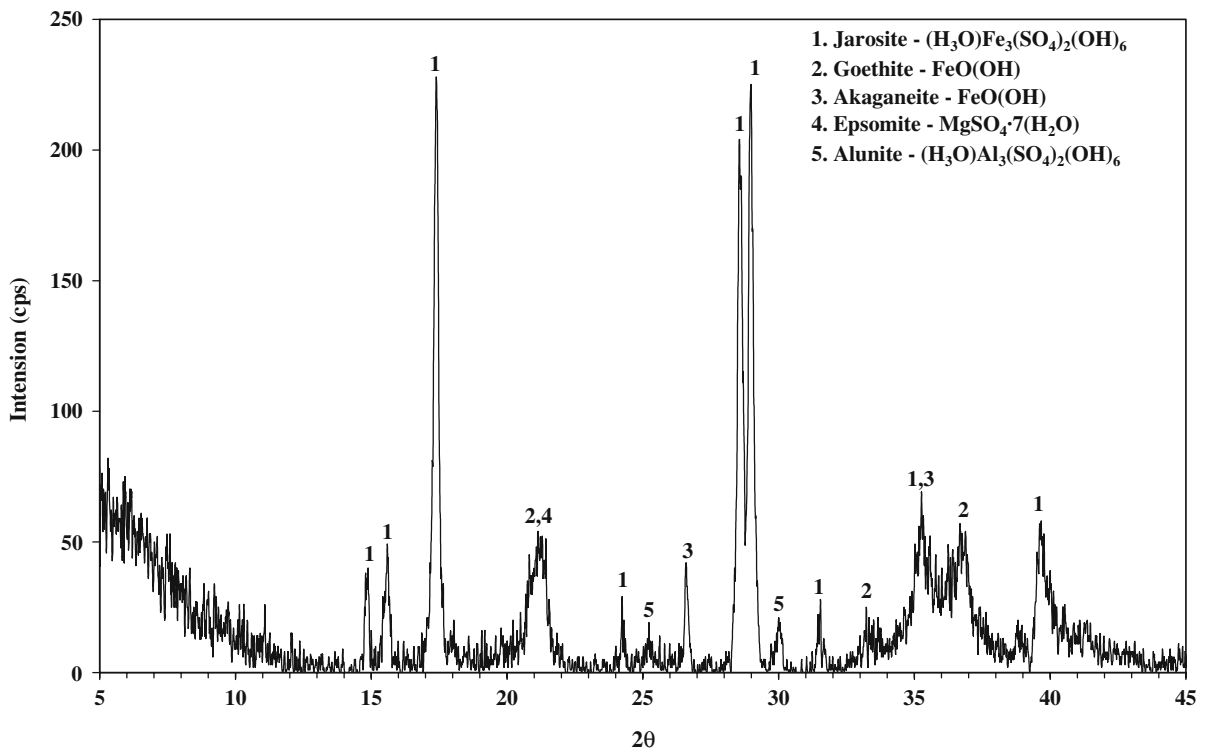
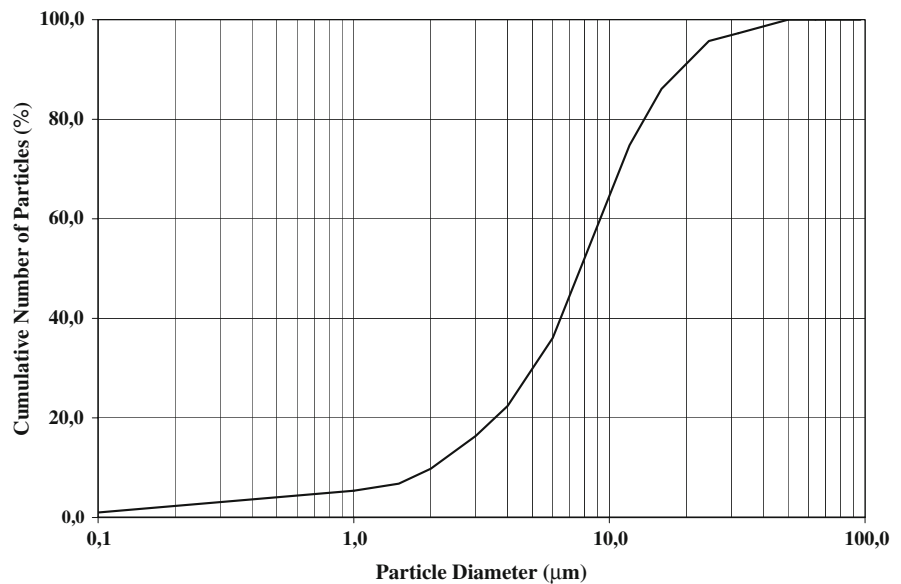


Fig. 1 Mineralogical phases of jarosite/alunite precipitate

Fig. 2 Particle size distributions of the jarosite/alunite residue by a laser scattering analyzer



For the study of the hydration products, the mortar pastes were obtained using the amount of water required to achieve normal consistency and a good workability. Then, they were cured in tap water at a temperature $20 \pm 2^\circ\text{C}$. At the ages of 28 and

90 days, the hydration was stopped by means of acetone and ether extraction. The hydration products were mineralogically determined by X-ray diffraction. XRD measurements were conducted with a Siemens D5000 diffractometer using nickel-filtered

Table 2 Dry mix compositions of mortars

Mortar	Mixing proportion (wt%)		
	Lime (powder)	Jarosite/Alunite	Sand
M ₀	30	0	70
M ₁	25	5	70
M ₂	15	15	70

CuK α 1 radiation (= 1.5405 Å), 40 kV voltage and 30 mA current.

TGA/DTA was used for the evaluation of the hydration rate [24]. A Mettler-Toledo TGA/SDTA 851 instrument was used. Type R thermocouple (Pt-13% Rh/Pt) was used for temperature measurements in this instrument. The samples were taken in a ceramic crucible and heated from room temperature to 900°C at a constant rate of 10°C/min in an atmosphere of carbon dioxide free nitrogen, flowing at 50 cm³/min. TGA/DTA were carried out simultaneously.

Finally, mercury intrusion porosimetry was considered a satisfactory technique for determining basic structural characteristics, such as pore size distribution, surface area and pore volume. A Carlo Erba 4000 mercury porosimeter was used for porosimetry measurements, having a pressure range from 1 to 4,000 bar.

3 Results and discussion

3.1 Properties of fresh mortars

The results of tests of fresh mortars properties (Table 3) show that the M₀ (lime-based) mortar

Table 3 Properties of fresh mortars

Mortar	Flow value (mm)	Air content (%)	Water demand (ml/kg)	Water retention (%)	Bulk density (g/cm ³)
M ₀	156	2.9	262.5	88.0	1.87
M ₁	162	3.0	220.0	88.5	1.94
M ₂	165	3.5	222.0	90.1	1.98

Table 4 Compressive and flexural strengths of hardened mortars

Mortar	Compressive strength (N/mm ²)		Flexural strength (N/mm ²)		Compressive to flexural strength (f_c/f_f)	
	28 days	90 days	28 days	90 days	28 days	90 days
M ₀	0.64 ± 0.05	2.10 ± 0.10	0.33 ± 0.01	0.84 ± 0.01	1.94	2.50
M ₁	1.20 ± 0.10	2.15 ± 0.10	0.50 ± 0.02	0.90 ± 0.02	2.40	2.39
M ₂	3.29 ± 0.10	3.53 ± 0.15	0.90 ± 0.02	0.95 ± 0.02	3.66	3.72

presents lower air content than the other two mixes. On the other hand, the addition of jarosite/alunite residue to lime mortar improves the density, as well as the water retention of fresh mortar. Furthermore, the mortars containing the above residue require about 16% less water than the reference lime mortar, to obtain the same flow. This fact can be attributed to the delayed hydration of the mortars with jarosite/alunite, due to its mineralogical composition. The water increase in the mortar is a combined effect of changes in particle size, density and physical and chemical reaction between water and solid particles. The replacement of lime with a by-product, which does not react with water, results to the decrease of the hydration rate and, consequently, to higher workability of the mortar.

3.2 Mechanical properties

The average results of compressive and flexural tests of hardened mortars, as well as the ratio of compressive to flexural strength (f_c/f_f) [18], are given in Table 4. From these results it can be seen that the reference lime mortar M₀ presented the lowest values at all ages. The addition of jarosite/alunite residue to lime mortar extremely increases the compressive and flexural strength of mortar. The rate of compressive strength development is higher at 28 days, followed by slower rate at 90 days.

At the age of 28 days, the mortar M₁ (16.6% lime substitution) presented 88% higher compressive strength and 52% higher flexural strength than the plain lime mortar. This increase is higher in case of M₂ mortar (50% lime substitution), where the compressive

strength is increased by 515%. Also the flexural strength of the mortar is considerably increased, by 270%. The rapid development of mortar strengths containing different jarosite/alunite replacement levels at 28 days indicates rapid hydration. Consequently, the increase in the compressive and flexural strengths of the mortars with curing time should be attributed to the hydration phenomena that take place. New hydration products are formed (by the addition of jarosite/alunite residue) that filled the pore spaces, thus refining the size of these pores. This observation was confirmed and by the mineralogical analysis (XRD) of hardened pastes. After 90 days of curing time the above differences are decreased and the compressive strength of the lime mortar M_0 reached 2.1 MPa. The corresponding value for M_2 mortar is 3.53 MPa.

All mortars present a low ratio of compressive to flexural strength (f_c/f_f), which suggests that those mortars are characterized by an elastic behavior, compatible with that of the original lime-based mortars. The ratio f_c/f_f of similar materials is proportional to the modulus of elasticity (E), for mechanical

measurements. A low f_c/f_f ratio corresponds to a low modulus of elasticity [18].

3.3 Mineralogical analysis of hardened mortars

The XRD patterns of the mortars M_1 (16.7% lime substitution) and M_2 (50% lime substitution), hydrated at 28 and 90 days, are presented in Figs. 3 and 4, respectively. $\text{Ca}(\text{OH})_2$, the main hydration product, appeared at 18° (2θ). Its peak of XRD was the highest at 28 days but was reduced thereafter due to the carbonation reaction, forming CaCO_3 . The carbonation started during the earlier drying phase, but contact with the atmosphere (and, of course, the presence of water) is what accelerates the process. Portlandite will later react with CO_2 from the air to form calcite by carbonation. Due to the dense structure of the hydraulic mortars, part of the portlandite from the interior will not be converted to calcite since moisture and CO_2 will not reach the interior of the mortar.

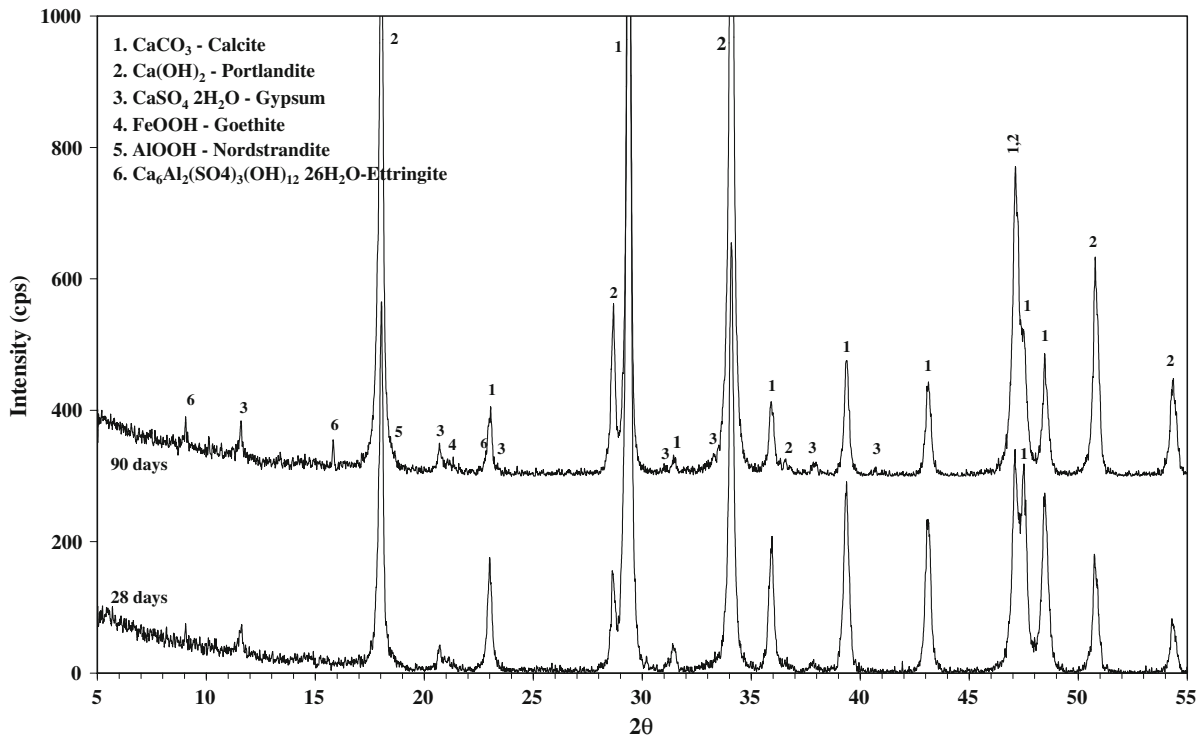


Fig. 3 X-ray diffraction of M_1 mortar at 28 and 90 days



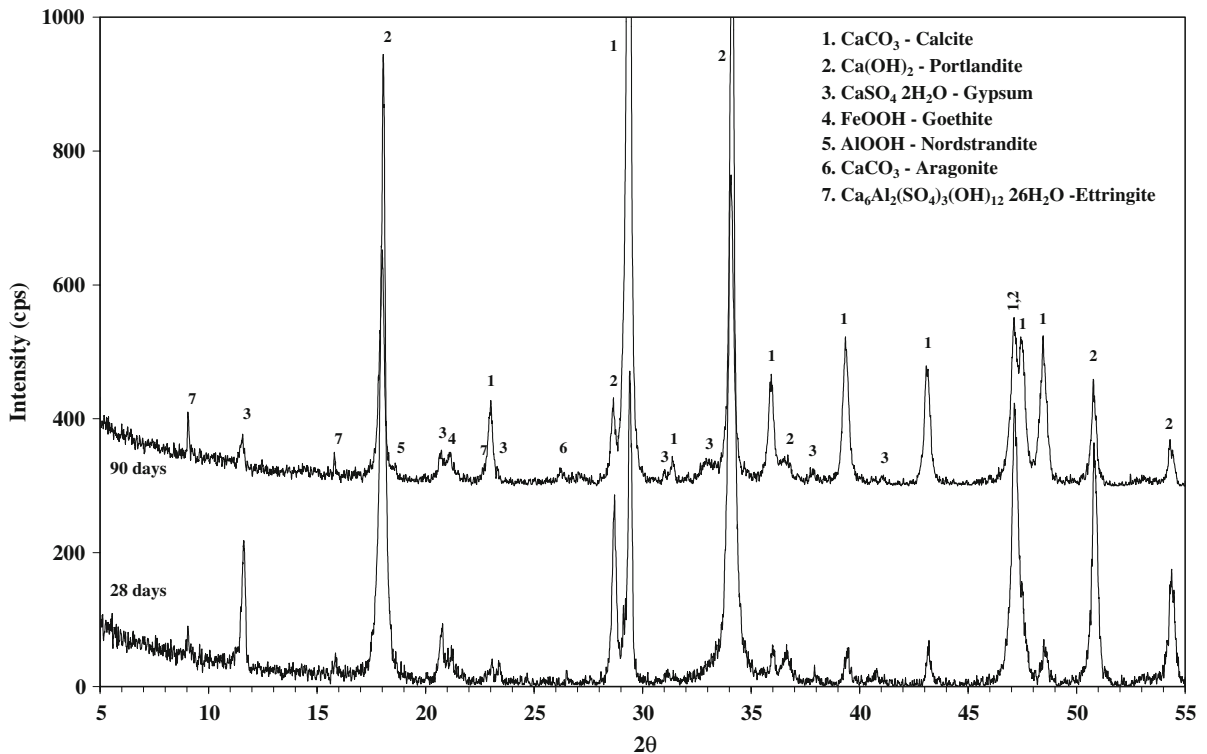


Fig. 4 X-Ray Diffraction of M_2 mortar at 28 and 90 days

It should be mentioned that XRD was unable to detect the jarosite/alunite phases (at the ages of 28 and 90 days), which obviously were dissolved in the high alkaline environment of the mortar. This fact was confirmed by the present of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, FeOOH and AlOOH , phases that were formed from the residue dissolution.

Strong peaks of gypsum exist at 28 days. The gypsum was formed from the $\text{Ca}(\text{OH})_2$, present in the mortar, and the sulphate from the residue. With progressive hydration gypsum and some of $\text{Ca}(\text{OH})_2$ are consumed, together with aluminum hydroxide in order to produce ettringite. The formation of ettringite needs gypsum, hydrated aluminates, portlandite and moisture. For both mortars with jarosite/alunite residue, an ettringite peak was observed at 9.1° (2θ). Its formation, together with the presence of gypsum, contributed to the improvement of the early mortars strength. The production of ettringite was maximized at 90 days.

According to the stability field diagram (Fig. 5) of the system $\text{CaO}-\text{Al}_2\text{O}_3-\text{SO}_3-\text{H}_2\text{O}$ [25] high sulphate concentrations stabilize gypsum and only when its

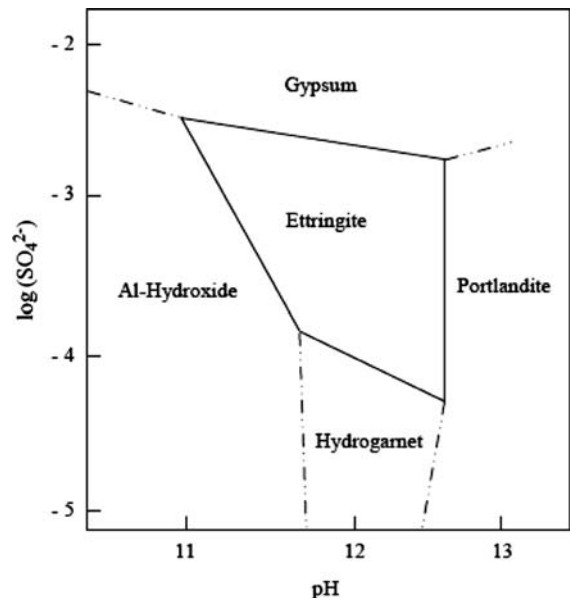
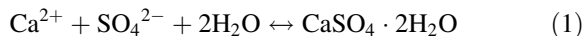


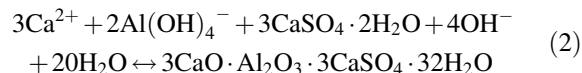
Fig. 5 Ettringite stability in alkaline environments [25]

concentration is decreased does ettringite become the stable phase. Water is especially important to ettringite formation because of the high water content

of the solid. When hydration is carried out in calcium hydroxide solutions, the amounts of gypsum are observed to decrease and those of ettringite to increase. At high sulphate concentrations, gypsum initially controls the maximum concentration of sulphate in solution by [26]:



Gypsum is used afterwards as a source of sulphate in the synthesis of ettringite according to the reaction given by:

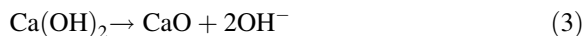


The drastic reduction of the amount of $\text{Ca}(\text{OH})_2$, due to the carbonation reaction and the formation of gypsum and ettringite, with a very fine microstructure, resulted to a pore refinement and a reduced permeability.

3.4 Thermal analysis

The results of the TG-DTA analysis of mortars M_1 and M_2 at 90 days, given in Figs. 6 and 7 respectively, confirmed the findings of the XRD analysis. The weight loss up to 110°C can be attributed to the removal of humid water. The endothermic peak at about 140°C, characterizing the dehydration of ettringite is very weak. The TG curve shows that a continuous heating rate originates a mass loss below 140°C, associated with the loss of the loosely bonded adsorbed water on the particle surface, which is accompanied with a small endothermic effect in the DTA curve. The endothermic peak at 180°C corresponds to the gypsum dehydration. The decomposition process of ettringite is observed at 250–290°C.

A weight loss at around 450°C can be attributed to the $\text{Ca}(\text{OH})_2$ dehydroxilation and the corresponding endothermic peak is due to the following reaction, which reveals the presence of $\text{Ca}(\text{OH})_2$:



The weight loss at 750°C is due to the CaCO_3 decarbonation. The endo-peak at 750°C is due to the following reaction:



Carbonation of a lime-mortar takes place when CO_2 dissolves in water and reacts with dissolved

calcium hydroxide. This reaction results in a calcium carbonate precipitation, due to the rapid supersaturation with respect to CaCO_3 in the solution existing in the mortar pores (which contains dissolved CO_2 and $\text{Ca}(\text{OH})_2$ in the condensed water).

3.5 Mercury porosimetry

For the determination of pore size distributions the cylindrical mathematical model (Washburns Equation) was employed to elaborate the results [27]:

$$P = -2K\cos(h)/r \quad (5)$$

in which “ r ” is the cylindrical pore radius, “ P ” is the pressure at which mercury enters into the pore, “ K ” is the surface tension of mercury (0.48 N/m at 25°C) and “ h ” is the contact angle between the mercury meniscus and a flat, nonmetallic surface ($\sim 140^\circ$). The results of total cumulative pore volume, specific surface area, pore radius average and bulk density, are summarized in Table 5.

In all cases the total pore volume decreased with the increase of curing time. For mortar containing only lime as a binder, the progressive increase in jarosite/alunite content reduced the pore volume from 220 to 190 mm^3/g (90 days), and consequently, bulk density was raised. The decrease of pore volume in case of plain lime mortar should be attributed to the lime carbonation. During carbonation calcite is deposited on the inside of pores but also at the entrance, thus clogging some of these pores and making them unavailable for mercury intrusion. The value for maximum volume intruded, in case of M_2 mortar (50% lime substitution), corresponded to an average pore radius of 415 nm. The corresponding value for plain lime mortar is 760 nm. These results indicate that hydration products may tend to fill up the larger pores found in lime. As previously noted, the addition jarosite/alunite led to the formation of gypsum and ettringite, during hydration and, consequently, the accumulated porosity was reduced and the compressive strength increased. This would explain why the addition of the jarosite/alunite residue generates a reduction in pore size in lime mortar. Furthermore, It should be noted that the porosity at 90 days of curing time of the both mortars with the above residue were almost the same or slightly lower, in case of 50% lime substitution.



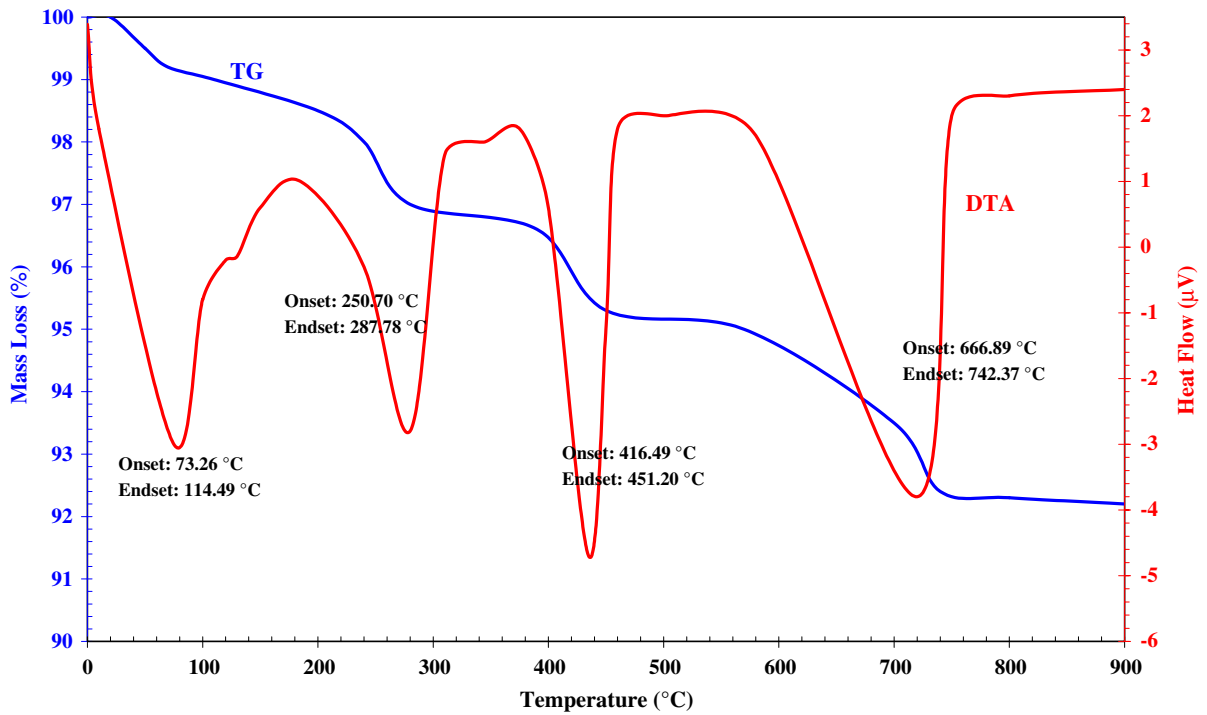


Fig. 6 T.G. and D.T.A. analysis of the M₁ mortar at 90 days

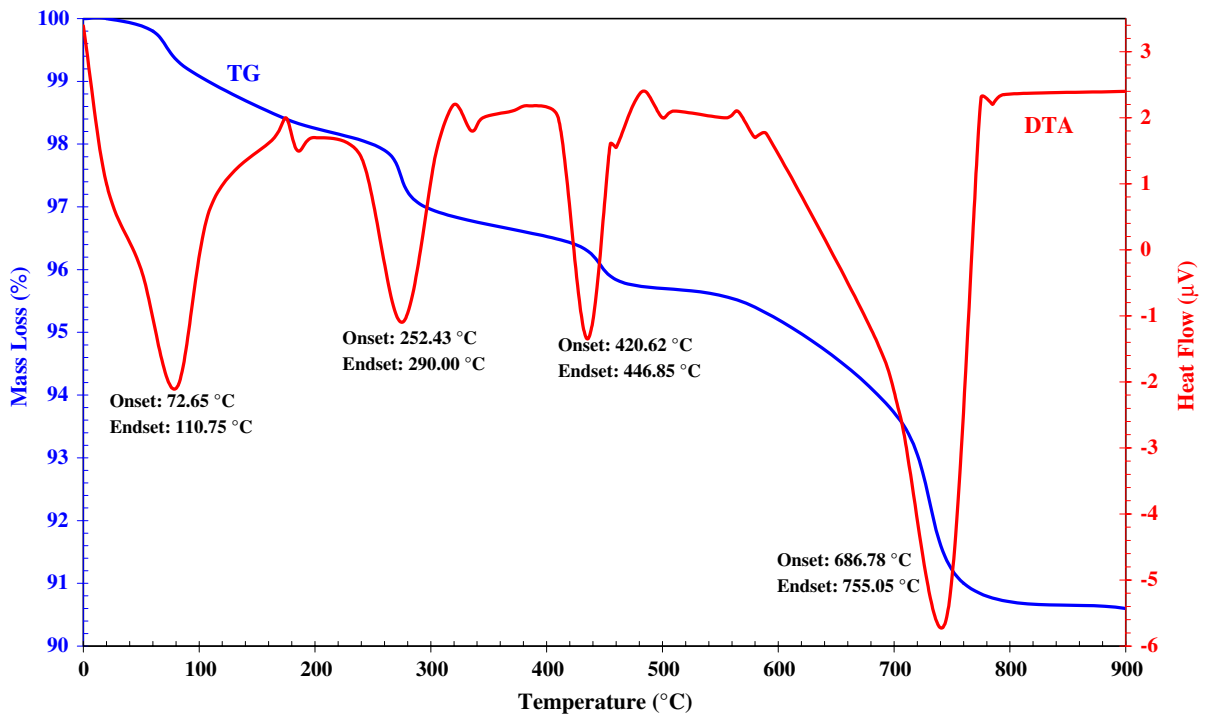


Fig. 7 T.G. and D.T.A. analysis of the M₂ mortar at 90 days

Table 5 Results from mercury porosimetry

Mortar	Pore volume (mm ³ /g)		Surface area (m ² /g)		Pore radius average (nm)		Bulk density (g/cm ³)	
	28 days	90 days	28 days	90 days	28 days	90 days	28 days	90 days
M ₀	239.8	222.6	3.43	3.56	775	760	1.61	1.65
M ₁	197.82	192.35	3.52	3.78	600	580	1.76	1.76
M ₂	197.93	191.93	4.58	4.86	440	415	1.81	1.82

4 Conclusions

The addition of jarosite/alunite residue up to 50%, in lime-based mortars, improved their mechanical properties. The produced mortars presented good workability, rapid and reliable setting and relatively lower porosity. More specifically:

- With the addition of jarosite/alunite residue, restoration lime-based mortars can be obtained with superior properties in fresh and hardened state, compared to the plain lime mortar. The necessary amount of water for the same workability of mixed lime mortars is much lower than this of plain lime mortar.
- The mortar M₂ (50% lime replacement) presented the highest compressive and flexural strengths, in comparison with the plain lime mortar. It also presented a low ratio of compressive to flexural strength (f_c/f_f). The obtained gain in compressive and flexural strength could be useful in case of masonry mortars when the demands for the compatibility of properties of restoration mortar to the properties of original lime-based mortar have to be met.
- The mineralogical analysis of the hydration products showed that the jarosite/alunite residue was dissolved in the high alkaline environment of the mortar, producing CaSO₄ · 2H₂O and AlOOH. During hydration, gypsum and some of Ca(OH)₂ are consumed, together with aluminum hydroxide in order to produce ettringite. The presence of gypsum and ettringite improved the mechanical behavior of the produced mortars at all ages.
- From mercury porosimetry results it was concluded that lime-based mortars reduced both their porous volume and their pore size as jarosite/alunite residue content in the mix increased. Higher reduction in porosity was observed in

mortar with 50% lime replacement, due to the hydration products. Longer curing times resulted in lower porosity values.

It is thus concluded that the jarosite/alunite residue, produced during hydrometallurgical treatment of nickel oxide ores with sulphuric acid, can be utilized as a raw material mortar restoration production.

References

1. Moropoulou A, Bakolas A, Aggelakopoulou E (2001) The effects of limestone characteristics and calcination temperature to the reactivity of quicklime. *Cement Concr Res* 31(4):633–639. doi:10.1016/S0008-8846(00)00490-7
2. Mosquera MJ, Silva B, Prieto B, Ruiz-Herrera E (2006) Addition of cement to lime-based mortars: effect on pore structure and vapor transport. *Cement Concr Res* 36(9):1635–1642. doi:10.1016/j.cemconres.2004.10.041
3. Moropoulou A, Bakolas A, Moundoulas P, Michailidis P (2000) Evaluation of compatibility between repair mortars and building materials in historic structures by the control of the microstructure of cement-based systems. *Concr Sci Eng* 2(8):191–195
4. Anagnostopoulos CA, Anagnostopoulos AC (2002) Polymer-cement mortars for repairing ancient masonries mechanical properties. *Construct Build Mater* 16(7):379–384. doi:10.1016/S0950-0618(02)00040-5
5. Moropoulou A, Bakolas A, Moundoulas P, Avdelidis NP (2000) Evaluation of compatibility between restoration mortars and traditional building materials by the control of the microstructure. In: Proc Conoscenze e Sviluppo di Criteri per la Definizione e Valutazione della Compatibilita nelle Malte per il Restauro, Scienza e Beni Culturali, Bressanone, pp 71–78
6. Rodriguez-Navarro C, Hansen E, Ginell WS (1998) Calcium hydroxide crystal evolution upon aging of lime putty. *J Am Ceram Soc* 81(11):3032–3034
7. Lanás J, Pérez Bernal JL, Bello MA, Alvarez JI (2006) Mechanical properties of masonry repair dolomitic lime-based mortars. *Cement Concr Res* 36(5):951–960. doi:10.1016/j.cemconres.2005.10.004
8. Moropoulou A, Bakolas A, Moundoulas P, Anagnostopoulou S, Aggelakopoulou E (2000) Compatible restoration mortars for the earthquake protection of Hagia Sophia. PACT, J Eur Study Group Phys Chem Biol Math Tech Appl Archaeol 59:29–51

9. Rota Rossi-Doria P (1998) Mortars for restoration: basic requirements and quality control. *Mater Struct/Mater Constr* 19(114):445–448
10. Moropoulou A, Cakmak AS, Biscontin G, Bakolas A, Zendri E (2002) Advanced Byzantine cement based composites resisting earthquake stresses: the crushed brick/lime mortars of Justinian's Hagia Sophia. *Construct Build Mater* 16(8):543–552. doi:[10.1016/S0950-0618\(02\)00005-3](https://doi.org/10.1016/S0950-0618(02)00005-3)
11. Moropoulou A (2000) Reverse engineering to discover traditional technologies: a proper approach for compatible restoration mortars. *PACT, J Eur Study Group Phys Chem Biol Math Tech Appl Archaeol* 58:81–107
12. Hendry AW (2001) Masonry walls: materials and construction. *Construct Build Mater* 15(8):323–330. doi:[10.1016/S0950-0618\(01\)00019-8](https://doi.org/10.1016/S0950-0618(01)00019-8)
13. Degryse P, Elsen J, Waelkens M (2002) Study of ancient mortars from Salassos (Turkey) in view of their conservation. *Cement Concr Res* 32(9):1457–1563. doi:[10.1016/S0008-8846\(02\)00807-4](https://doi.org/10.1016/S0008-8846(02)00807-4)
14. Agatzini-Leonardou S, Dimaki D (1994) Recovery of nickel and cobalt from low-grade nickel oxide ores by heap leaching with dilute sulfuric acid at room temperature. Greek Patent No: 910100234
15. Agatzini-Leonardou S, Dimaki D (2001) Method for extraction of nickel and/or cobalt from nickel and/or cobalt oxide ores by heap leaching with a dilute sulfuric acid solution, prepared from sea water, at ambient temperature. Greek Patent No: 1003569
16. Agatzini-Leonardou S, Oustadakis P, Zafiratos J (2000) Removal of aluminum and chromium from nickel–cobalt sulfate solutions. Greek Patent No: 1003419
17. USEPA (1994) Method 1311: toxicity characteristic leaching procedure, test methods for evaluating solid wastes physical/chemical methods. United States Environmental Protection Agency
18. Moropoulou A, Bakolas A, Moundoulas P, Aggelakopoulou E, Anagnostopoulou S (2005) Strength development and lime reaction in mortars for repairing historic masonries. *Cement Concr Compos* 27(2):289–294. doi:[10.1016/j.cemconcomp.2004.02.017](https://doi.org/10.1016/j.cemconcomp.2004.02.017)
19. Sarp Tunçoku S, Emine Caner-Saltık N (2006) Opal-A rich additives used in ancient lime mortars. *Cement Concr Res* 36(10):1886–1893. doi:[10.1016/j.cemconres.2006.06.012](https://doi.org/10.1016/j.cemconres.2006.06.012)
20. EN 196-1 (1994) Methods of testing cement—determination of compressive strength
21. EN 1015 (1998–2002) Methods of test for mortar for masonry, parts 1–19
22. EN 1015-3 (1999) Methods of test for mortar for masonry—determination of consistence of fresh mortar (by flow table)
23. EN 1015-11 (1999) Methods of test for mortar masonry—determination of flexural and compressive strength of hardened mortar
24. Bakolas A, Aggelakopoulou E, Moropoulou A, Anagnostopoulou S (2006) Evaluation of pozzolanic activity and physico-mechanical characteristics in metakaolin-lime pastes. *J Therm Anal Calorim* 84(1):157–163. doi:[10.1007/s10973-005-7262-y](https://doi.org/10.1007/s10973-005-7262-y)
25. Hampson CJ, Bailey JE (1982) On the structure of some precipitated calcium alumino-sulphate hydrates. *J Mater Sci* 17(11):3341–3346. doi:[10.1007/BF01203504](https://doi.org/10.1007/BF01203504)
26. Álvarez-Ayuso E, Nugteren HW (2005) Synthesis of ettringite: a way to deal with the acid wastewaters of aluminium anodising industry. *Water Res* 39(1):65–72. doi:[10.1016/j.watres.2004.07.029](https://doi.org/10.1016/j.watres.2004.07.029)
27. Pirard R, Alie C, Pirard JP (2002) Characterization of porous texture of hyperporous materials by mercury porosimetry using densification equation. *Powder Technol* 128(2–3):242–247. doi:[10.1016/S0032-5910\(02\)00185-7](https://doi.org/10.1016/S0032-5910(02)00185-7)