

# Effectiveness of Olivine-Rich Ultrabasic Rocks from Greece on Acid Mine Drainage and Dairy Wastewater Treatment

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## Abstract

The present study is referred to the utilization of olivine-rich ultrabasic rocks from two ophiolitic rock occurrences; harzburgite of Megaplatanos of Locris area, central Greece, and dunite of Skoumtsa, Kozani prefecture, northern Greece. The aim of the study is to investigate the usage of such rocks in environmental applications and especially as neutralization agents of dairy wastewater (DW) and acid mine drainage (AMD) from mixed sulfides metallurgical industry or mine sites. DW and AMD are two of the most problematic industrial derivatives due to their content in hazardous substances e.g. organics, heavy metals, toxic chemicals. On the other hand, olivine (the main component of dunite and harzburgite) is a well-known mineral used to solve such environmental issues.

The experiment on AMD was conducted at laboratory batch conditions mixing separately two different synthetic AMD solutions with variable concentrations of metals and powder samples of the two different rock-types of similar grain size (<0,25mm). Eh and pH values and Zn, Pb, Cu, and Fe concentrations indicate that the Megaplatanos harzburgite was moderately responded, in contrast to the Skoumtsa dunite that reacted effectively. Moreover, heavy metal uptake capacity rises noticeably in the more diluted in metals solution. Consequently, dunite can be used potentially as a passive way treatment of AMD, by neutralizing and removing heavy metals from the solution, opposed to harzburgite that may only be used as a first step in the treatment of AMD.

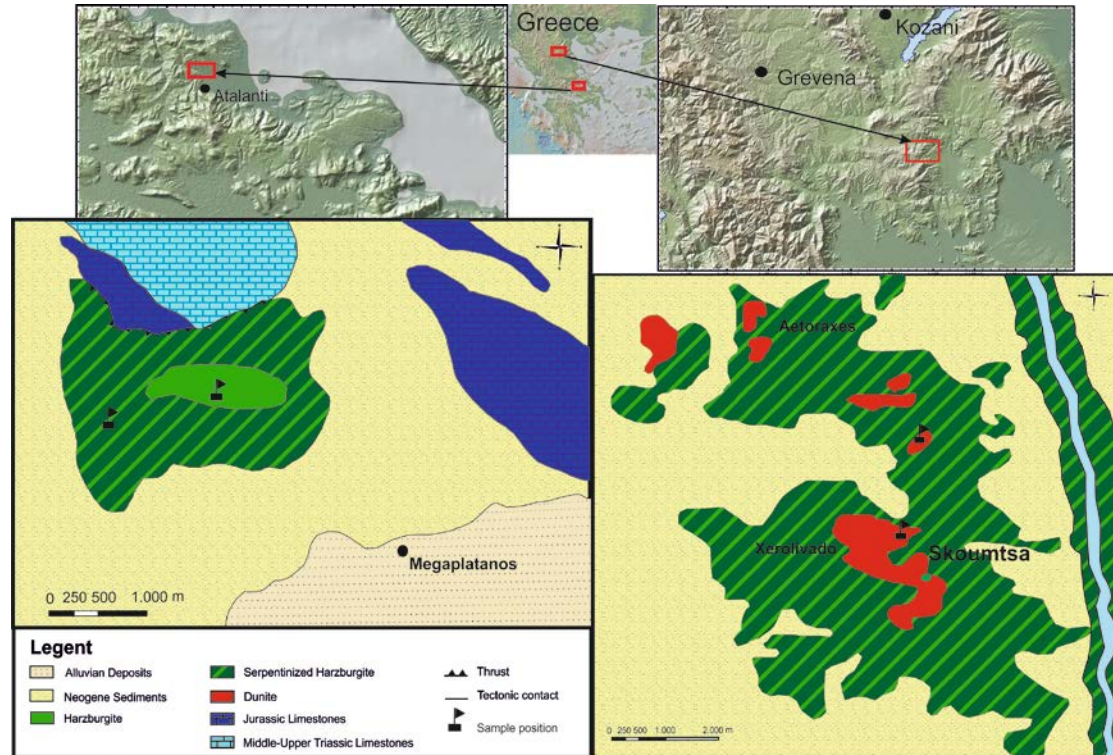
As it concerns the acid whey, the experiment was conducted in columns reacting four different compositions of whey with two different grain size fractions of Skoumtsa dunite. Several chemical and physical parameters were daily measured on dunite flour and filtrates before and after treatment for a week. The pH measurements showed that the final solution gain in alkalinity, reaching almost neutral to slightly alkaline values. The COD values were not the desirable ones relatively to EU standards. Thus, the obtained pH values encourage usage of dunite for the treatment of DWs, but further investigation is required, especially under pilot or demonstration scale conditions.

## Introduction

Dairy wastewater (DW) and acid mine drainage (AMD) originated from metal mines and industries are two of the most problematic industrial waste derivatives due to their content in hazardous substances e.g. organics, heavy metals, toxic chemicals [1,2-3, 13-14, 17,23]. The most environmentally important form of the DW is acid whey, a major byproduct of milk, yogurt and cheese industries. The whey cannot be dispensed to the environment due to its severe pollution effect, as this is measured by the two oxygen-depletion indices of COD and BOD (Chemical and Biochemical Oxygen Demand respectively), which show relatively high values. The COD ranges from 50.000 to 80.000 mg/l, and the BOD between 30.000 and 50.000 mg/l [2,3, 23]. The whey, depending on the productive

process and the precipitation of casein, is distinguished in acidic whey (pH<5) and sweet whey (pH=6-7) [2,3,23]. It is charged with high organic load, consisting of lactose (70-72% of total solids), soluble proteins (8-10% of total solids), lipids and NaCl, KCl (12-15% of total solids) [23], and 93% of water [17]. AMD refers to the outflow of acidic water from metallurgical industries or mine sites, mostly as a result of oxidation of metal sulfides by the combined action of air, water and bacteria. It is characterized as a dilute solution of sulfuric acid, with low-pH (1.5-3.5), significant amounts of dissolved Fe and high concentrations of heavy and toxic metals, such as Cu, Zn, Pb, harmful for any biological activity [1,13-14]. As the direct uses for AMD fluids are non-existent, while the current whey usages are very limited, alternative treatments are necessary. Several natural mineral and rocks usually after small scale industrial processing are able to treat polluted waters separating useful solids and producing clean water that can be reused or discharged safely.

The magnesium silicate mineral olivine has been proposed to solve several environmental issues, especially those related to AMD handling [6, 10-12, 20, 22]. However, while dunite, an ultrabasic peridotitic rock consisting almost solely from olivine, has been the subject of extensive research worldwide as neutralizer of acid waters, harzburgites, another olivine-rich peridotitic rock more abundant than dunite, which except olivine, comprises orthopyroxene in its composition, has taken less attention for this specific application. The main focus of the current research relies on the effectiveness of dunite for DW treatment, whereas the second aim of the study is to investigate a harzburgitic rock for AMD management. The effectiveness of dunite and harzburgite is also compared. For these purposes, olivine-rich ultrabasic rocks from two different ophiolitic sequences were selected (Fig. 1). The first location belongs to the Locris ophiolitic body in central Greece, where the occurrence of harzburgite nearby the Megaplatanos village has been studied. The second location is at the eastern part of the Vourinos ophiolite complex in northern Greece, where the ore-deposit of Skoumtsa, Kozani prefecture, is developed. The deposit is mined by Thermolith S.A. mining company and the olivine-rich product is mainly used in refractories.



**Fig. 1:** Geological sketch maps and sampling locations in Megaplatanos, Atalanti and Skoumtsa, Kozani areas

## Materials and Methods

The analyzed rock samples were selected in such a way that they represent unaltered mantle peridotites. Polished thin sections were first prepared in order to thoroughly examine the specific mineralogical and textural characteristics of each sample. The modal mineralogy was determined with a polarizing microscope and X-Ray Diffraction (XRD). Scanning electron microscopy (SEM) using EDS analysis were carried out in order to determine the chemical composition of certain mineral phases. Whole-rock analyses for major elements were carried out using XRF or ICP-MS methods.

For the mixing-neutralizing experiments four representative rock samples (Megaplatanos: MG1; Skoumtsa: CSK1, CSK2 and CSK3) were selected. The different grain-sizes of each sample used, are given below: MG1= $<0.25\text{mm}$ , CSK1= $<0.25\text{mm}$ , CSK2= $0.25\text{-}0.75\text{mm}$ , CSK3= $0.75\text{-}2.00\text{mm}$ . The mixing experiments were realized in the laboratories of the Faculty of Geology and Geoenvironment, NKUA under ambient conditions.

In order to achieve maximum control of the experiments for AMD neutralization treatment, two different  $\text{H}_2\text{SO}_4$  synthetic solutions (SYS1 and SYS2), instead of natural AMD, were used. The two simulating to AMD synthetic solutions, the more concentrated in metals and  $\text{H}_2\text{SO}_4$  solution SYS1 and the more diluted in the same metals and  $\text{H}_2\text{SO}_4$  solution SYS2, have been mixed conical flasks under stirring with similar grain size ( $<0.25\text{mm}$ ) powder samples of the two different rock-types: Skoumtsa dunite (CSK1) and Megaplatanos harzburgite (MG1). Measurements conducted at solutions before the batch experiment and at the final filtrates include pH, Eh, and metal concentration by AAS technique. The solid product of the reaction (flour) was investigated using XRD, XRF, SEM and SEM-EDS methods.

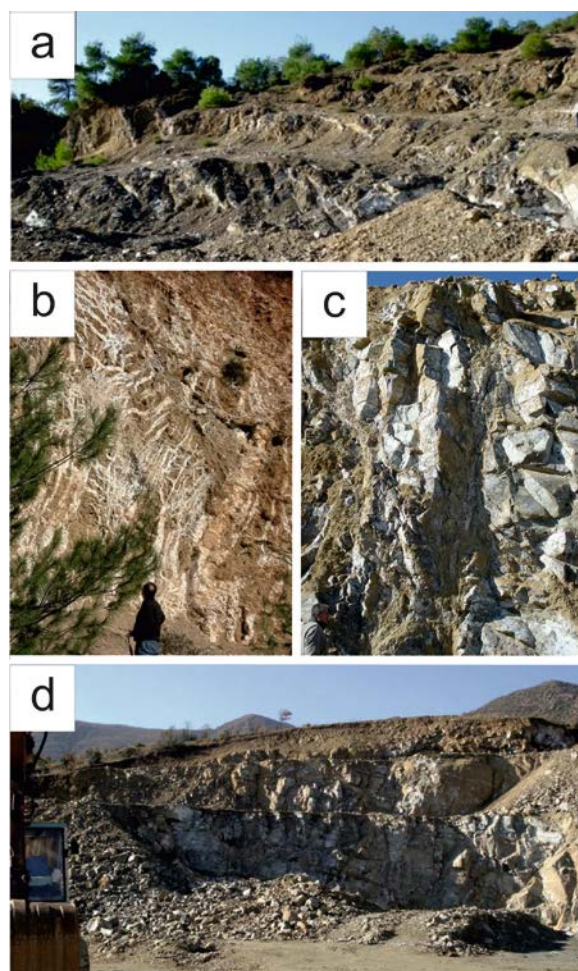
The whey-rock mixing experiment was conducted in columns at laboratory conditions and without stirring. Four different compositions of whey from OLYMPUS S.A. and FAGE S.A. dairy companies and two different grain size fractions of dunite from Skoumtsa were used. In particular, OLY1 and OLC2 are the wheys from the production of yogurt and cheese respectively of Olympus dairy products. FM1 and FM2 are the pre- and post-condensation wheys respectively from the production of milk in the Fage dairy plant. Several chemical and physical parameters were daily measured on dunite flour and filtrates before and after treatment for a week. XRD, SEM-EDS and XRF measurements for the flour of Skoumtsa dunite were conducted, while for the filtrates their pH, Eh and COD values were measured.

## Geology and Petrology of Megaplatanos Harzburgite and Skoumtsa Dunite

One rock-type we used for our experiments is a harzburgite occurring near the village of Megaplatanos, Atalanti, Locris. The Megaplatanos ultrabasic body is part of the western Neotethyan ophiolitic belt situated along the western margin of the Pelagonian zone of Greece and belongs to the Sub-Pelagonian zone. It comprises a west-verging thrust sheet dominated by ultrabasic rocks emplaced over Lower Triassic – Middle Jurassic, thick-bedded carbonate formations. and covered by the younger formations of the geotectonic unit of Eastern Greece and in particular the neritic limestones of Upper Cretaceous, flysch and marly rocks of Neogene age [7-8]. The ophiolitic rocks in Megaplatanos area extent at about  $4.5\text{km}^2$  and consists of variably serpentinized massive harzburgite and minor dunite pods (Figs. 1, 2). The degree of serpentinization of the ultrabasic rocks differs greatly, with the highly-serpentinized harzburgites displaying dark-green to black color. Stockwork of numerous magnesite dykes and veinlets penetrate harzburgite and dunite locally (Fig. 2a, b). A sparse network of pyroxenite veins of some millimeters to some centimeters in thickness also cross-cut both ultrabasic rocks. Fault-controlled tectonic breccia occasionally appear within harzburgite.

The other rock we used for our experiments is a dunite, which is cropping-out near the village of Skoumtsa, Vourinos Mt., Kozani (Figs. 1, 2). The Vourinos ophiolite contains a harzburgite–dunite

dominated peridotite and a preserved overlying crustal succession whose pseudostratigraphy dips steeply to the west [5, 18, 21]. Dunite bodies present within the harzburgite are either deformed into the dominant peridotite foliation or undeformed, crosscutting the foliation. The overlying crustal succession contains, from bottom to top, gabbroic cumulates with minor plagiogranites, a sheeted dyke complex (Asprokampos dykes) and locally hypabyssal and extrusive mafic rocks (Krapa series) [5, 16, 18, 21]. Sampling was performed to the eastern part of the Vourinos ophiolite, which is dominated by serpentinized dunite and harzburgite (Fig. 2c, d). The degree of serpentinization varies from minimum to high. Sparse disseminated chromitite horizons are present within the dunitic bodies. Pliocene-Pleistocene sediments overlie ultrabasic rocks. Locally, harzburgite is covered by Quarternary deposits (mainly erosion products of ultrabasic rocks).

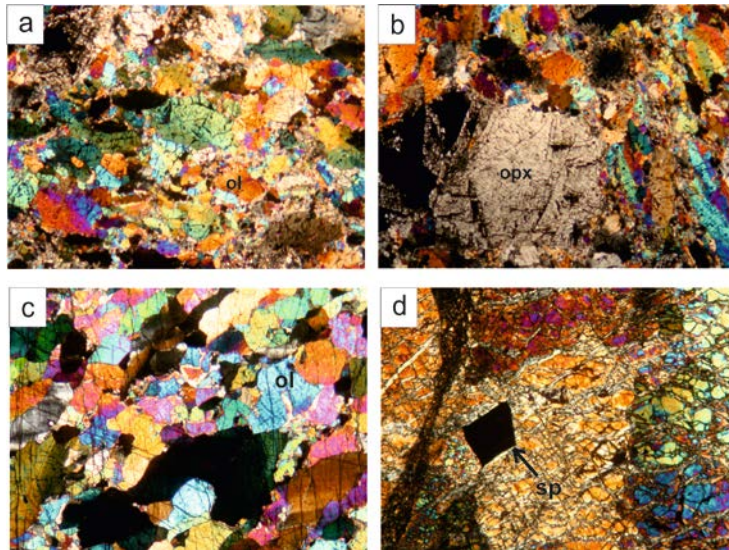


**Fig. 2:** Photographs from the ultrabasic rock occurrences in Megaplatanos area (a, b) and Skoumtsa area (c, d). Magnesite dykes crosscut massive harzburgite (a), dense network of magnesite veins (stockwork) within dunite and harzburgite (b), massive dunite outcrop (c) and an open pit dunite quarry (d)

The primary minerals of harzburgite from Megaplatanos and Skoumtsa are olivine (65-80 vol.%), orthopyroxene (15-30 %), clinopyroxene (3-5%) and Cr-spinel (< 5%). The amount of serpentine, which is the dominant secondary phase in harzburgite, ranges from below 5% up to about 70%. Mylonitic to porphyroclastic textures are prevail. Olivine porphyroclasts (<2 mm) are usually elongated and exhibit well-developed undulatory extinction and strain lamellae. Olivine also occurs as smaller polygonal neoblasts (~0.2 mm) with 120° triple junctions, which generally surround porphyroclasts of orthopyroxene (Fig. 3a,b). The latter commonly have lobate boundaries and show undulatory extinction, bending and kinking. These structures are typical features of Alpine-

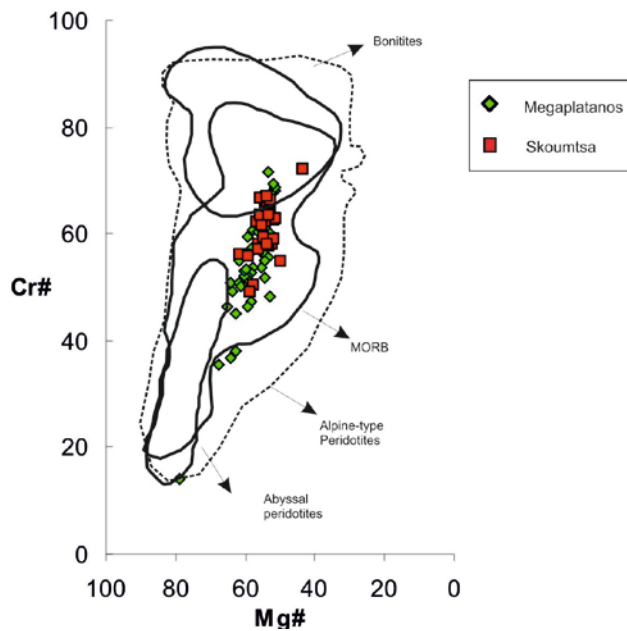
type upper-mantle peridotites that have suffered cataclastic to plastic high-temperature deformation. Dark-brown colored Cr-rich spinels commonly form euhedral to anhedral grains (<3mm). They are usually found as interstitial crystals or within olivine, while rarely enclose small early formed olivine crystals.

The dunite contain olivine (85-90 vol.%), orthopyroxene (up to 5%) and disseminated spinel (up to 10%). They are fresh to weakly serpentinized. They display granular to porphyroclastic texture dominated by stretched, elongated olivine grains with undulatory extinction and kink bands as a result of plastic deformation (Fig. 3c,d). During serpentinization mesh texture has also developed, while small chrysotile veins up to 0.05 mm in length cross-cut the rock. Orthopyroxene usually shows exsolution lamellae of clinopyroxene, while dark-brown spinel forms mostly euhedral and more rarely subhedral disseminated crystals.



**Fig. 3:**Microphotographs from polarizing microscope under crossed polars of representative samples from Megaplatanos (a, b), and Skoumtsa (c, d). (a) Porphyroclasts of elongated deformed olivine and orthopyroxene crystals, (b) orthopyroxene porphyroclast, displaying smaller polygonal olivine neoblasts at its margins, (c) undulatory extinction in deformed olivine crystals, (d) euhedral spinel crystal within olivine of a serpentinized dunite (mesh texture). Length of view for pictures (a), (b) and (d) 0.6mm, for picture (c) 2mm

Two representative whole rock chemical analyses of dunite and harzburgite from Skoumtsa and Megaplatanos area respectively are shown in Table 1. In spite of the two rocks show similar chemical composition, dunite is slightly more enriched in MgO than harzburgite, while the opposite is noted for CaO, Al<sub>2</sub>O<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub>. The analyzed olivine, spinel and orthopyroxene of the studied samples are chemically homogeneous and do not display any distinctive zoning. Their forsterite content of olivine is slightly higher in the dunite (Fo<sub>90.95-93.04</sub>) than in the harzburgite (Fo<sub>90.04-92.67</sub>), while not any significant compositional difference between porphyroclasts and neoblasts has been observed. Orthopyroxene in the studied dunite, and harzburgite is enstatite, while few clinopyroxene is diopside. Variability in spinel compositions is illustrated in a Cr# vs. Mg# diagram (Fig. 4). The Cr# [=100\*(Cr/(Cr+Al))] of the spinel's dunite CSK1 ranges from 49.30 to 72.24, while for harzburgite MG1 from 35.44 to 71.56. Similarly, its Mg# [=100\*(Mg/(Mg+Fe))] for CSK1 ranges between 43.40 to 61.58 and for MG1 from 51.54 to 78.85.



**Fig. 4:**Cr# vs Mg# plot for spinels of samples MG1 and CSK1

**Table 1.** Whole rock major element analyses for harzburgite (MG1) from Megaplatanos (analysis by ICP-MS, ACME Laboratories, Canada) and for dunite (CSK1) from Skoumtsa (XRF analysis provided by THERMOLITH S.A., Chalkidiki, Greece), nd = not detected.

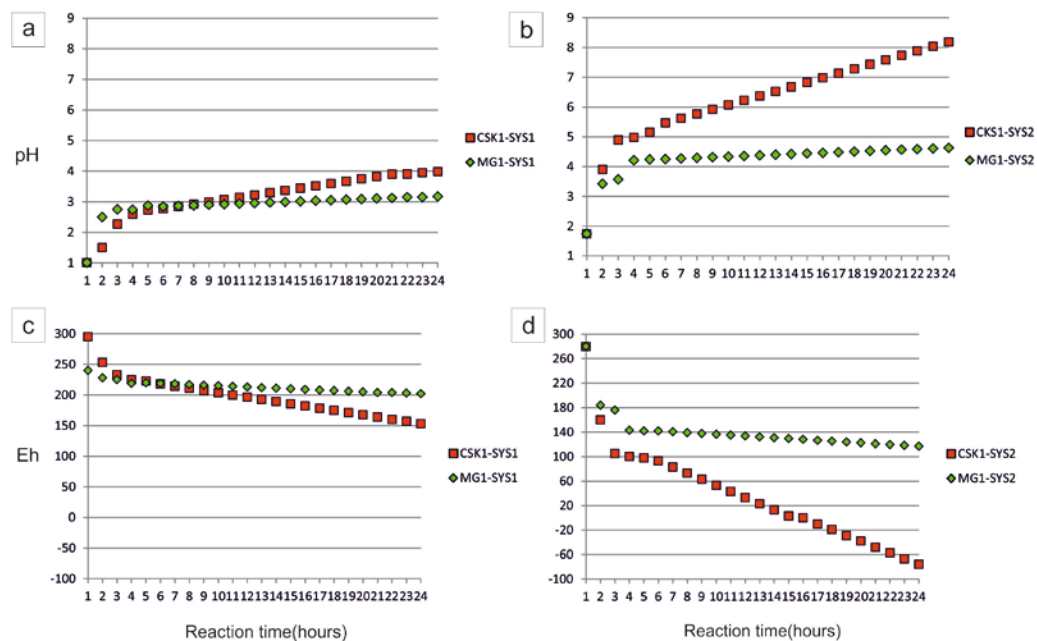
Sample	MG1	CSK1
SiO <sub>2</sub>	42.85	43.50
TiO <sub>2</sub>	<0.01	nd
Al <sub>2</sub> O <sub>3</sub>	0.65	0.30
CaO	0.68	0.40
Cr <sub>2</sub> O <sub>3</sub>	0.432	nd
Fe <sub>2</sub> O <sub>3</sub>	9.45	8.1
K <sub>2</sub> O	<0.01	nd
MgO	45.94	46.20
MnO	0.131	nd
Na <sub>2</sub> O	0.17	nd
P <sub>2</sub> O <sub>5</sub>	0.01	nd
LOI	0.00	0.8
<b>Total</b>	100.32	99.30

## Waste and rock mixing – Experiments and results

### *Experiments on acid mine drainage*

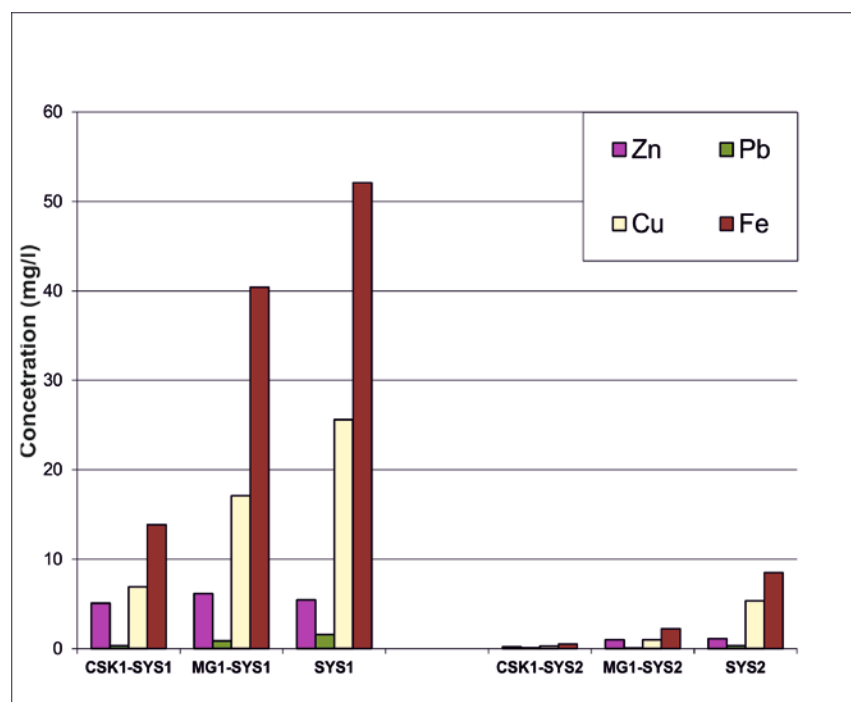
The physicochemical characteristics pH and Eh, as well as the concentrations in H<sub>2</sub>SO<sub>4</sub> and heavy metals of the initial synthetic solutions SYS1 and SYS2 have as follows: (SYS1) pH=1.01, Eh=309mV, [H<sub>2</sub>SO<sub>4</sub>]=0.055M, [Cu]=25mg/l, [Pb]=1.5mg/l, [Fe]=500mg/l and [Zn]=5mg/l; (SYS2) pH=1.74, Eh=280mV, [H<sub>2</sub>SO<sub>4</sub>]=0.01M, [Cu]=5mg/l, [Pb]=0.3mg/l, [Fe]=100mg/l and [Zn]=1mg/l. The two batch treatment experiments that were conducted at laboratory temperature (~25° C) comprise: (1<sup>st</sup> Experiment) reaction of 50ml SYS1 with 5gr olivine rock (MG1 and CSK1) grain size <0.25mm, 96 hours duration time, 250rpm stirring; (2<sup>nd</sup> Experiment) reaction of 50ml SYS2 with 5gr olivine rock (MG1 and CSK1) grain size <0.25mm, 48 hours duration time, 250rpm stirring. Measurements for pH and Eh regarding the olivine-rich flours dissolved with water display an average pH of 9.5 for MG1 and 9.7 for CSK1, and an average Eh of -143mV for MG1 and -158mV for CSK1.

The monitoring of output solution chemistry in the experiments showed that after 24 hours pH increased from 1.01 to 4 and to 3.22 after the reactions of SYS1 with CSK1 and MG1 respectively. The initial pH=1.74 of the solution SYS2 firstly neutralized and then even became slightly alkaline at 8.21 in the 24 hours treatment with CSK1, while with MG1 increased only to 4.61 (Fig. 5). Moreover, SYS1 initial Eh=309mV dropped to 153mV after 24 hours treatment with CSK1 and to 202 mV after 24 hours treatment with MG1. SYS2 initial Eh=280mV after 24 hours reached -84mV after treatment with CSK1, and 116mV after treatment with MG1 (Fig. 5).



**Fig. 5:** Comparative diagrams of pH and Eh vs. reaction time for mixing CSK1 and MG1 with SYS1 (a, c), and SYS2 (b, d). pH increase and Eh decrease in all cases are clearly shown

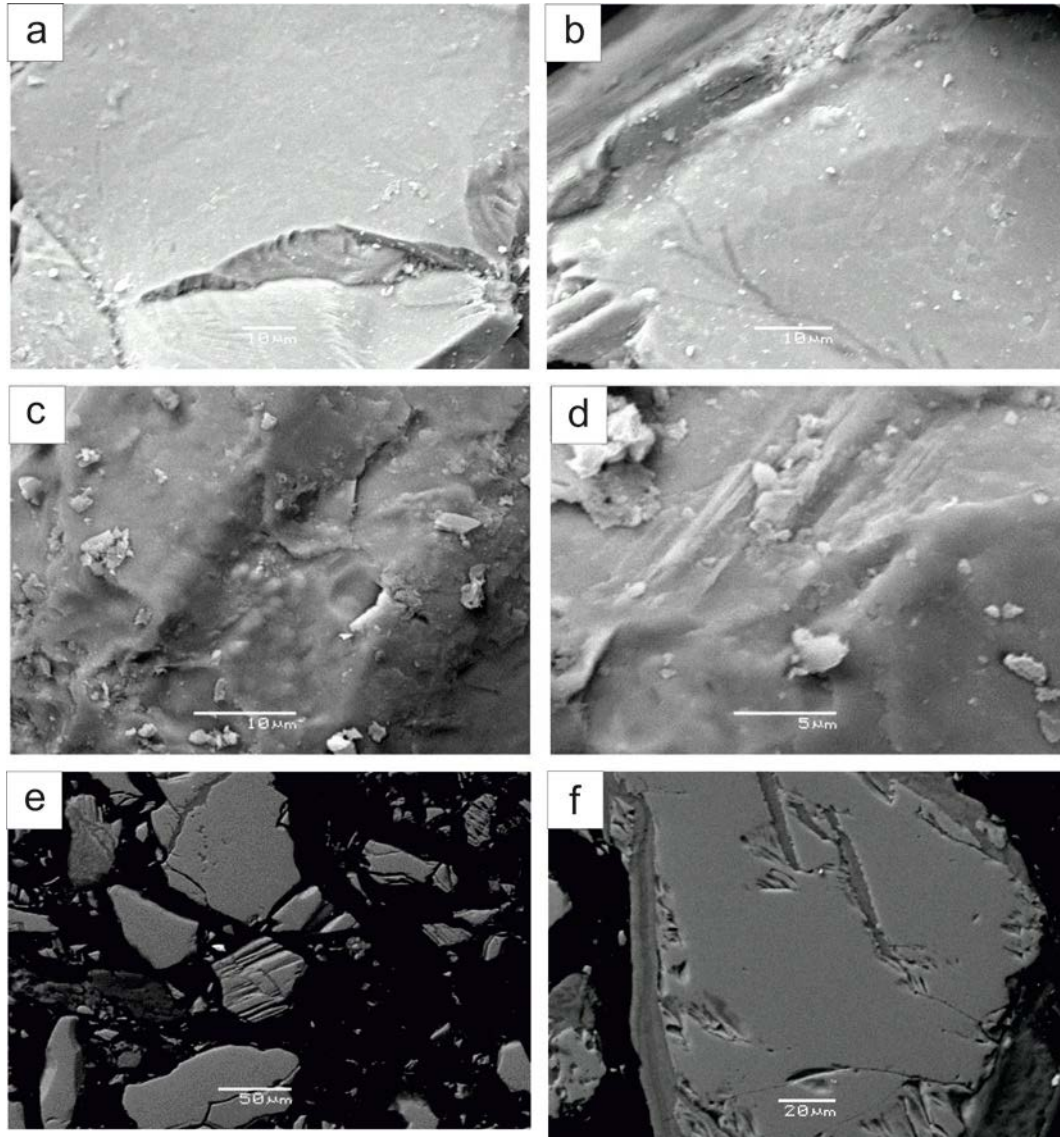
The initial [Zn] that SYS1 was 5.44mg/l decreased after its reaction with CSK1 to 5.07mg/l, while with MG1 increased to 6.15mg/l (Fig. 6). For the solution SYS2 [Zn] decreased from 1.1mg/l to 0.01 mg/l after the reaction with CSK1 and to 0.99mg/l with MG1. Regarding [Pb], for SYS1 it was 1.59mg/l initially, while after the reaction decreased with CSK1 to 0.32mg/l and with MG1 to 0.83 mg/l. The initial [Pb] for SYS2 was 0.34mg/l and decreased to 0.08mg/l after the reactions with both CSK1 and MG1. [Cu] initially was 25.6mg/l for SYS1, whereas after its reaction with CSK1 decreased to 6.9mg/l and to 16.9mg/l with MG1; for SYS2 from 5.34mg/l decreased considerably to 0.3mg/l and to 0.93mg/l respectively. For [Fe] the initial value of SYS1 of 521mg/l and dropped to 138.5mg/l after the reaction with CSK1 and to 404mg/l with MG1; for SYS2 from 85mg/l, also dropped to 0.01 mg/l for CSK1 and to 22.1mg/l for MG1



**Fig. 6:** Zn, Pb, Cu, Fe/10 concentrations before and after reactions. At the left the samples CSK1 and MG1 reacted with SYS1 and at the right with SYS2

SEM images show that after reactions the surfaces of olivine and pyroxene crystals are somehow disturbed

and subparallel dissolution troughs and rough edges are developed (Fig. 7e, f). SEM-EDS analyses show that olivine chemistry in dunite and harzburgite is also affected to some extent. After reactions, olivine grains in dunite are slightly poorer in magnesium, with its MgO content decreasing from 92.76 to 91.41. Regarding harzburgite, there is no obvious difference, with Fo<sub>91.28</sub> before the reaction, and Fo<sub>91.33</sub> after it. Furthermore, olivine rims are slightly depleted in Mg relatively to its cores after reactions. At the center of grains, concerning MG1 Fo<sub>91.20</sub> to Fo<sub>92.04</sub> and for the boundaries the values decrease Fo<sub>90.74</sub> to Fo<sub>91.74</sub>. For CSK1, at the center Fo<sub>91.59</sub> to Fo<sub>92.37</sub> and at the boundaries Fo<sub>90.82</sub> to Fo<sub>92.18</sub>.



**Fig. 7:** SEM microphotographs of olivine and pyroxene grains before any treatment (a, b) and after the reaction with a whey (c, d) and an AMD simulating solution (e, f) after the reaction with SYS acid drainage. Olivine in (c) and (d) is embedded in resin. Olivine is shown in (a-e) and pyroxene in (f). See more in the text

#### *Experiments on dairy wastewater*

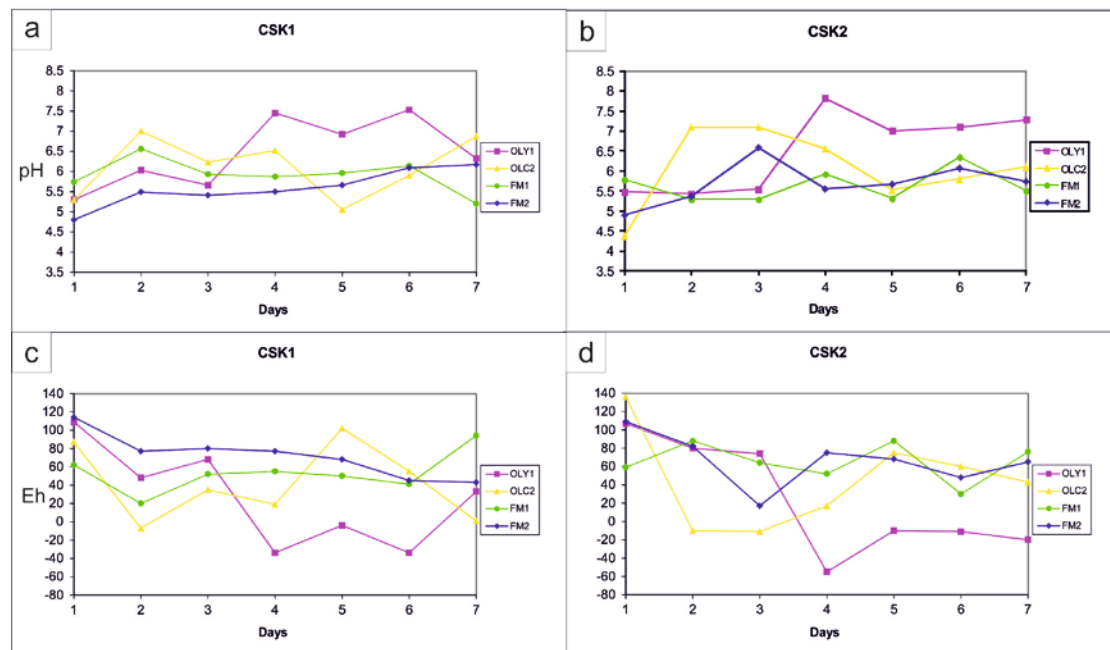
The initial compositions and physical characteristics of the wheys, which were given by the respective factories, have as follows: The whey OLY1 from the production of yogurt from OLYMPUS S.A. dairy plant is estimated to contain lipids, lactose, proteins, inorganic salts and less than 5% of solids. It displays white color, low viscosity and disagreeable odor. The cheese whey OLC2 is estimated



to contain slightly more solid ingredients. It displays yellowish color, low viscosity and very heavy odor. The FM1 whey was taken from the first separator during the milk production of the FAGE S.A. dairy plant. It comprises 5% of solid ingredients, 4.5% lactose, 0.5% proteins, 3% lipids, and 0.2-0.3% inorganic salts (personal communication). It displays white color, high clarity, noticeable odor and relatively high viscosity. The FM2 condensed whey has six times more solids than FM1 and reduced water content. It presents yellow color, very high viscosity and bubbles and foam at its surface.

The reaction treatment was taken place in burettes/columns, in which 80g of dunite flour formed two successive layers. The lower layer was always 30g of the sample CSK3 (grain size 0.75 to 2.00mm), while the rest 50 g was either powder from the sample CSK1 (grain size 0.00-0.25mm) or from the sample CSK2 (grain size 0.25-0.75mm). 80ml of the 4 different types of whey (samples OLY1, OLC2, FM1 and FM2) were poured into the burettes.

The duration of the experiment was a week, while pH and Eh measurements were taken in the filtrates after reactions, as well as in an untreated part of the wheys, every 24 hours. For the untreated whey OLY1 initial pH values ranged from 4.07 to 4.20 during the week. After the reaction with CSK1 pH values ranged from 4.88 to 7.53, with the biggest value to be found at 6<sup>th</sup> day, while the pH of CSK2 ranged from 4.93 to 7.81, with the biggest value to be found at 4<sup>th</sup> day (Fig. 8a, b). Regarding Eh, its range was from 148 to 156 mV for the untreated whey, while after the reaction with CSK1, Eh values ranged from -34 to 109 mV, with the smaller values found at the 4<sup>th</sup> and 6<sup>th</sup> day (Fig. 8c, d). With CSK2 Eh ranged from -55 to 107 (smallest value was noted on the 4<sup>th</sup> day). For OLC2 initial pH values ranged from 3.36 to 3.62. After the reaction with CSK1 pH values ranged from 5.05 to 7.00, with the biggest value to be found at 2<sup>nd</sup> day, while at CSK2 pH was from 4.39 to 7.10, with the biggest value to be found at 2<sup>nd</sup> and 3<sup>rd</sup> days. Regarding Eh, the initial range was from 183 to 192 mV. After the reaction with CSK1, Eh values ranged from -7 to 102 mV, with the smaller values found at the 2<sup>nd</sup> day, while at CSK2 Eh ranged from -11 to 136 mV, with the smaller value to be noted at 3<sup>rd</sup> day. For FM1 initial pH values ranged from 4.38 to 4.59.

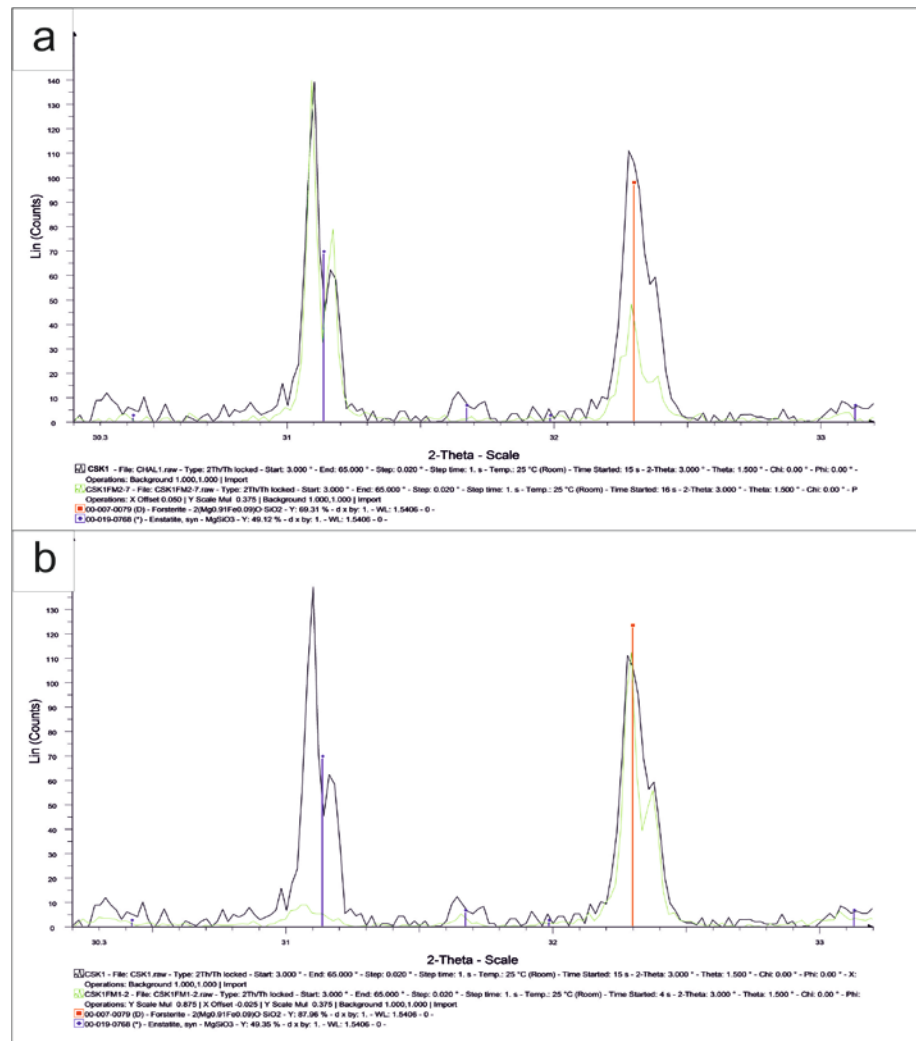


**Fig. 8:** Comparative diagrams of pH and Eh vs. reaction time in days for mixing CSK1 and MG1 with the four wheys. See text for discussion

After the reaction with CSK1 pH values ranged from 5.2 to 6.56, with the biggest value to be found at 2<sup>nd</sup> day, while CSK2 pH values ranged from 5.29 to 6.35, with the biggest rate to be found at 6<sup>th</sup> day.

Regarding Eh, the initial range was from 124 to 139 mV. After the reaction with CSK1, Eh values ranged from 20 to 94 mV, with the smaller value found at the 2<sup>nd</sup> day, while at CSK2 Eh ranged from 30 to 88 mV, with the smaller value to be noted at 6<sup>th</sup> day. For FM2 initial pH values ranged from 4.06 to 4.20. After the reaction with CSK1 pH values ranged from 4.80 to 6.17, with the biggest value noted at 7<sup>th</sup> day, while CSK2 pH values ranged from 4.91 to 6.59, with the biggest value noted at 3<sup>rd</sup> day. Regarding Eh, the initial range was from 148 to 154 mV. After the reaction with CSK1, Eh values ranged from 43 to 114 mV, with the smaller value noted at the 7<sup>th</sup> day, while at CSK2 Eh ranged from 17 to 109 mV, with the smaller value noted at 3<sup>rd</sup> day. For the whey FM1 the value of COD was also measured before and after the treatment with the mixture of CSK3+CSK2. The initial COD value was 56000 mg/l and the final 52300 mg/l (at pH=6.35 and Eh=30).

XRD and SEM measurements were realized in the rock powder used before and after the treatment with the wheys. It is generally observed that new minerals were not formed, the relative intensities of the present minerals were changed, as well as there was a slightly relocation of main peaks (Fig. 9). Regarding to the chemical analysis of olivine grains, a lower forsterite component was observed after reaction. More specifically, before the reaction, olivine has values from Fo<sub>90.04</sub> to Fo<sub>93.67</sub>, with an average Fo<sub>92.76</sub>, while after the reaction, grains are slightly poorer in magnesium, with values from Fo<sub>88.73</sub> to Fo<sub>93.30</sub>, and average Fo<sub>91.21</sub>. Moreover, olivine grains present after reactions with the whey ruff surfaces (Fig. 7c, d) instead to the smoother ones before treatment (Fig. 7a, b).



**Fig. 9:** Representative XRD patterns after the reaction of dunite with the two milk wheys. (a) Decrease of enstatite peaks after reaction of CSK1 with FM2, (b) Depletion of olivine peaks after reaction of CSK1 with FM1

## Discussion

### *Effectiveness of the rock types studied on acid mine drainage treatment*

Acid mine drainage problem combines high sulphate levels – acidity and also high concentration of heavy metals that poses the greatest environmental risk. The treatment of this problem is a major and immediate task where active or abandoned mines and metallurgical sites and factories with unused ore or slug stock piling or discharges exist. A large number of organic and inorganic filter materials and several methods for the remediation of AMD have been provided, and a lot of money for research on it has been spent [24 and references therein]. However, none of the suggested methods is fully satisfactory, especially when is applied to industrial scale. The most frequently used techniques include AMD reaction with lime, limestone or calcium silicate from slag of steel industries. At first all these techniques include neutralization of AMD, achieving pH in the range from 6 to 9 [9]. The absorption and then precipitation of toxic heavy metals or other contaminants is further achieved using mostly cation exchange resins, constructed wetlands or sulfate-reducing bacteria. The utilization of olivine (the dominant mineral at harzburgite and dunite) in AMD treatment, though it has been described for neutralization and filter mostly for Cu by some investigators [6, 9, 11, 20], has not thoroughly studied as absorbent of other heavy metals such as Zn, Fe, and Pb.

The acid neutralization capacity of the studied olivine flours is illustrated in Fig. 5a, b, which shows the pH of the suspension as a function of reaction time for two different in heavy metals concentrations synthetic solutions (SYS1 and SYS2) and two different in mineralogy and origin solid agents (MG1 and CSK1). The results for the denser in metals solution SYS1 show that the pH in 24 hours increased from 1.05 to 4.00 when it reacted with the dunite CSK1 and to 3.22 with the harzburgite MG1, meaning that pH remains acidic after the reaction for both materials. For the 2<sup>nd</sup> experiment of SYS2 with initial pH equals to 1.74, CSK1 sample changes pH after 24 hours to 8.21, while for MG1 pH increases just to 4.61, meaning that the richer in olivine sample CSK1 reaches neutral to slightly alkaline values after the reaction, while the lower in olivine content sample MG1 pH is converted to moderately acidic only. From the results, we conclude that the effectiveness at neutralization rises as the solution dilutes, with the more dilute solution (SYS2) attaining better pH values than SYS1. As a consequence, the results in pH change are not so encouraging regarding harzburgite (MG1) and are much better at dunite (CSK1), probably due to the presence of larger amounts of pyroxenes and larger content of Ca, Al and Fe in harzburgite.

Redox potential (Eh) on the other hand, controls the solubility of metals and identifies whether the conditions in the water, ground or any other material are reducing (negative potentials) or oxidizing (positive potentials). It also predicts the states of different chemical species in the water, such as dissolved metals. For example, at air-lacking areas, such as submerged soils, swamps and marine sediments, redox potential displays negative values suggesting reducing environment. In opposite aerated materials or liquids like fresh, sea or acid mine waters, usually indicate oxidizing conditions. The results of the present study indicate the redox conditions, which were oxidizing for both solutions SYS1 and SYS2, became more reducing – however remaining positive – after their reactions with both CSK1 and MG1 samples. It deserved to be noted that for SYS2 the initial Eh value of 280 mV became negative at -84 mV after 24 hours reaction with sample CSK1, suggesting a clear reducing environment, while with the sample MG1 it was less decreased at the positive value of 116 mV. Thus Eh shows better response to dunite than to harzburgite, probably due to the same abovementioned reasons. This is also indicated by the reciprocal variability of Eh to pH in the reaction products and the changing of Eh values to negative when pH was greater than 7.

The amount of heavy metals retained by the two flours is calculated from the difference between the amount of metals initially present in the synthetic solutions and the amount remaining in solution after filtering. Thus, the degree of metal retention, represented by %Retained, can be expressed as a unit-less fraction according to the following equation [11]:

$$\% \text{Retained} = 100 \times \frac{([X]_i - [X]_f)}{[X]_i}$$

where  $[X]_i$  is the initial concentration of Cu, Zn, Pb, Fe and  $[X]_f$  is concentration of Cu, Zn, Pb and Fe in the filtrate. Table 2 shows the percentages of retention of Cu, Zn, Pb and Fe for the reactions between the two different solutions with the two flours. For the reaction of CSK1 with SYS1, values are clearly decreased, with the retention percentages about 80%, apart from Zn with a percentage of 2.4%. After the reaction of CSK1 with SYS2 Zn, Cu and Fe retained almost totally and Pb retained by about 80%. Regarding metals retention by the sample MG1 the obtained data show greater decrease at about 80% for Pb and Cu and about 70% for Fe when it reacted with the more diluted in metals solution SYS2. The final retentions of all metals after the reaction of MG1 with the more concentrated in metals solution SYS1, as well as the Zn retaining in the reaction MG1+SYS2, are inadequate not exceeding 50%. All these results are shown also in the graph of Fig. 6, in which we can additionally see the clear decrease in the contents of almost all metals during both experiments.

**Table 2.** Heavy metals percentage of retained elements from liquid. The percentage is calculated with the type:  $\% \text{Retained} = 100 * ([X]_i - [X]_f) / [X]_i$ , where X: Cu, Zn, Pb, Fe, i=initial, f=final.

	CSK1-SYS1	CSK1-SYS2	MG1-SYS1	MG1-SYS2
Zn %Retained	2.4	99.1	-	12.6
Pb %Retained	80.5	79.4	45.9	82.4
Cu %Retained	76.6	99.8	33.2	81.8
Fe %Retained	76.0	99.9	17.5	67.8

Regarding observations with the electronic microscope, aim to show any erosional distortion at the external surface of minerals in the ultrabasic rocks but also to investigate any changes at their chemistry after the reactions with the synthetic solutions. From the Fig. 7e,f the dissolution seems to affect, at least partly, both olivine and pyroxenes. Their surfaces have been locally etched creating elongated subparallel troughs and rough edges, possibly due to dissolution followed lattice imperfections, such as dislocations – mostly in olivine, which has already suffered high temperature deformation expressed as undulatory extinction and strain lamellae - or cleavage, in the pyroxenes. Regarding the reaction products, it is known that the surface area of the adsorbent is chemically affected by the liquid. Hydroxyl-bearing substances e.g.  $\text{Si}(\text{OH})_4$ , hydroxyl-sulphates and amorphous or colloid products, like opal or goethite are produced at the surface layer of olivine [4, 6, 9, 10, 12]. The creation of amorphous products depends on several factors such as temperature, grain size, quantity of olivine and acid concentration [15]. Nevertheless, our SEM study reveals that olivine after treatment has not developed, apart from flat surfaces and dissolution channels, any crusts of a new substance or an obvious thick residue or chemical zoning. This probably happens because of low concentration of these products on the surfaces, which are not detectable from our SEM instrument, or due to the reaction products have been removed along with the effluent and/or during preparation of the probe inserted in the SEM.

Conclusively, as indicated in the previous paragraphs, dunite (CSK1) from Skoumtsa is a better material for the treatment of AMD for both pH neutralization and metal adsorption from the solution and can be effectively used as a passive way treatment, unlike harzburgite (MG1) from Megaplatanos that may only be used as a first step in the treatment of AMD, by causing a small increase in pH and some decrease in concentrations of the heavy metals. In other words, dunite that is of almost pure olivine is a much more efficient toxic metal remover and neutralization agent than other ultrabasic materials, that additionally to olivine, comprise other minerals.

#### *Effectiveness of the rock types studied on dairy wastewater treatment*

The utilization of olivine (the dominant mineral of harzburgite and dunite) in neutralizing organic wastes such as whey from dairy industries is as far as we know an innovative project. Despite of the

different possibilities of whey utilization, a big amount of whey produced worldwide and also in Greece is discarded without treatment. Most of the cost-effective treatment techniques are focused in physicochemical and/or biological methods as coagulation, flocculation, aerobic/anaerobic digestion, due to large organic load [2].

Dairy whey is the liquid remaining by the manufacture of dairy products and displays high values of COD and BOD. It mainly consists of lactose, soluble proteins, lipids and mineral salts (e.g. NaCl, KCl and CaCl<sub>2</sub>). Casein precipitation leads to the formation of two whey types: acidic whey (pH<5) and sweet whey (pH=6-7) [2,3,23]. In the present study, the four different wheys are acidic with pH ranging from 3.36 to 4.59. pH measurements showed that although the initial pH values were relatively low, the final solutions generally gain in alkalinity, reaching almost neutral to slightly alkaline values. However fluctuations in the pH values for some wheys are observed during the week. Therefore, OLY1 and OLC2 (yogurt and cheese wheys respectively) reach neutral to alkaline values, while FM1 and FM2 (normal and concentrated milk wheys respectively) almost neutral values. The best performance from all wheys is noted to yogurt and concentrated milk wheys, as in both pH increased considerably after the 3<sup>rd</sup> day. The behavior of the various wheys on neutralization cannot easily explained. The easily recognized different parameters and characteristics of the wheys, e.g. composition, density, concentrations of ingredients and viscosity, perhaps play the most important role in obtaining acceptable pH values. In opposite, the variability in grain size between CSK1 (<0,25mm) and CSK2 (0.25-0.75mm) that lead to different contact surfaces between the reactants, seems not to affect substantially the pH values measured at the final solutions (Fig. 8a, b). This fact means that the effectiveness in neutralizing the acidity of wheys does not depend very much on the size fraction of the rock used, at least when the grain size is less than 0.75mm. Thus we can say that it is not necessary for a dairy industry to use ultra-fine-grained rock, which normally is of higher cost.

The steady oxidizing character of all four untreated wheys is clearly depicted at their Eh values, which remains constantly positive, ranging from 124 to 192 mV, during the whole week that the experiments were taken place. After the treatment, Eh values are decreasing, reaching even negative values (up to -55 mV) and therefore reducing conditions in the effluent after yogurt whey treatment (Fig. 8c, d). Also, it deserved to be noted that the most acidic whey responded faster relative to the less acidic ones, such as OLC2 that at 2<sup>nd</sup> day reached neutral pH and negative values of Eh, while OLY1 reached neutral pH and negative values of Eh at the 4<sup>th</sup> day.

COD is a vital importance parameter to be measured. The COD values given in the literature for wheys differ largely, depending on several factors of production. They usually range between 50.000-80.000mg/l [2]. The chosen sample for COD measurement was FM1 reacted with CSK2. The initial value before the reaction was 56.600 mg/l, while after the treatment with the dunite flour was measured at 52.300 mg/l. This very small change of 7.5%, is insufficient taking in mind that the COD value of the EU directives is 125 mg/l maximum. Thus our results on the oxygen demand for management of the biogradable and non-biodegradable oxidizable pollutants of the whey, that is what COD test indicates, were not encouraging, remaining in unacceptable levels.

As concerns the optical result in SEM scale of the olivine crystals after dunite reacted with the wheys, dissolution marks, similar to those described by Grandstaff [4] and Van Herket. al. [22], are obvious (Fig. 7c, d). Initial dissolution takes place in restricted areas of olivine surface, causing small changes at the external morphology of crystals, with etching peaks [4, 6], suggesting that the material does not response homogenously to the dissolution. The analysis of those distorted areas, showed depletion of Mg relative to Si. Microanalysis, showed that olivine is slightly poorer in Mg at his surface. There are also small differences of MgO content between the core(Fo<sub>91.37</sub>- Fo<sub>93.75</sub>) and the rim(Fo<sub>90.02</sub>- Fo<sub>92.13</sub>)of olivine grains. On the other hand, from XRD patterns, we can observe that for CSK1 with OLY1, OLC2, and FM1, the main impact is a clear decrease of the main enstatite peak, while for FM2 there is a decrease of forsterite peak. Concerning CSK2 with OLC2 and FM2, the results are different, with an increase of enstatite, while at OLY1 and FM1 there is no obvious difference (Fig. 9). The

observed minor changes in olivine chemistry and olivine/orthopyroxene ratio are probably due to differences in the dissolution rates of the minerals and the type of the whey.

From all above, the present study give promising results and can be a good basis for additional research over the dunite material as a confrontation against the main hazardous byproduct of dairy industries. However, this research on organic wastewater treatment, as well as on acid mine drainage remediation have to be also realized in a greater scale, either constructing pilot plants within the laboratory or in even better doing on-site demonstration experiments. Additionally, any further technical investigation should take under consideration the economic dimension of the study materials and infrastructure needed in relation to the anticipated results.

## Conclusions

Eh, pH and AAS measurements show that harzburgite responses moderately concerning acid mine drainage treatment, while dunite shows promising results and reacted more effectively. This behavior seems to be attributed rather to the presence of orthopyroxene in the harzburgite, than the major element chemistry of the rocks, which in our experiments was quite similar. pH values remain acidic to moderately acidic during harzburgite reaction with the more concentrated in metals and acid solution, while better results in acidity are attained when the reaction proceeds with the more diluted solution. During the reaction of dunite with the more concentrated solution pH remains acidic, and reaches neutral values when dunite reacts with the more diluted solution. Regarding heavy metal adsorption, the degree of retention displays a strong positive correlation with pH. The harzburgite is capable of retaining significant amounts of Cu, Zn and Fe, even when exposed to relatively high initial metal concentrations of the more concentrated solution, but responses quite well when more diluted solutions involved. Therefore, the absorption is almost complete at the reaction of dunite with the diluted solution and moderate with the concentrated solution. Probably, different liquid/solid ratio will end in more excited results.

For the dairy wastewater issue, Eh and pH measurements showed that the final solutions (after the reaction) reach more friendly to the environment values in relation to the unacceptable ones that the untreated industrial byproduct show. The yogurt and cheese wheys response highly to the reaction, while the normal and concentrated milk wheys response moderately. In particular, the former wheys reach neutral to alkaline values, while the later almost neutral values. The increase in pH most likely depends on one or more easily recognized physicochemical characteristics of the wheys, e.g. initial concentration of their various ingredients, origin, density and viscosity. In spite of rock grain size less than 0.75mm is adequate for obtaining good pH results, the measured COD values were far away from EU standards.

SEM-EDS and XRD measurements show that the reactions taken place in the experiments for acid mine drainage and dairy wastewater treatments affected the surfaces of the mineralogical constituents of the rocks involved, creating characteristic etching features along crystal edges, internal lattice dislocations or cleavage planes. Also during the experiments slight changes in olivine chemistry and olivine/orthopyroxene ratio are observed.

As a final outcome, harzburgite, which is a common ultrabasic rock in Greece and elsewhere, cannot be considered as an efficient material for acid mine drainage and dairy wastewaters treatment. Instead, dunite, a less abundant ultrabasic rock, can be used effectively both in passive way remediation of acid mine drainage, by neutralizing and removing heavy metals from the solution, as well as in dairy wheys, by neutralizing them. Thus, the more Mg-rich olivine in the reactant materials, the better environmental results in the treatment of acid mine drainage and dairy wastewaters.

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