BE-6036

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SYNTHESIS REPORT

A. INTRODUCTION

A.1 SPECIFICATION OF THE INDUSTRIAL PROBLEM

Programmes conducted for o considerable time to investigate moulding sends have resulted in major improvements in foundry sand practice. Silica has been c satisfactory aggregate material of foundry send. The use of olivine as a moulding sand is not widdly spread and it is applied in castings where the use of silica sand is problematic. The best example is the production of austenitic manganese steel. where the system MnO-SiO_2-FeO forms o low melting point eutectic and the consequent reactions result in a pitted steel surface. By replacing silica no such eutectic is formed_ The shift from silica send to no-silica aggregates - zircon sand, chromite sand and olivine sand - has several advantages, especially from an environmental point of view. Olivine sand for economical reasons is better placed to replace silica send in more confine foundry sands. A shift from silica - sand towards olivine in foundry applications due to tighter environmental constrains in the E.U. is expected to result in a great demand for olivine in the relevant industry.

Another new application of olivine, which is proposed is this project, is its use as o neutralizing agent for the industrial. waste acids. Today, the common practice for the neutralization of the waste acids is by the addition of limestone, which leads to the production of gypsum. This gypsum finds no industrial application while its disposal is problematic from the environmental point of view. The proposed olivine process leeds to the production of valuable by-products (silicagel - fine grain magnetite and Mg-sulphate) and leaves no waste products, which makes the process economically and environmentally attractive.

In Hellas, there exist huge "reserves of olivine sources (dunites, harzburgites, mining tailings], which are connected with existing magnesite and chromite mining activities in Northern Hellas. In fact, there is not quarrying cost for these dunites - hurzburgites, sine'e they derive as by products from the main mining activity.

A.2 OBJECTIVES

The objectives of the present research programme were as follows :

- Location of large deposits with the most promising olivine source rocks (e.g. low pyroxene harzbourgites, < 10wt% serpentinized dunites) and/or dunite tailings. from existing magnesite ond chromite mining operations.
- Production of olivine concentrates suitable for the foundry industry through beneficiation and/or calcination tests.
- New applications of olivine sand in the field of quality castings
- Further development and optimization of the neutralization process of industrial waste acids by olivine.
- Development of new technologies for the chemical treatment of residues and industrial waste aimed forwards improvement of recycling and reduction of environmental problems. For example production of silica gel by reaction of olivine with industrial waste acids to be used in new industrial applications.

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B. TECHNICAL OVERVIEW

The project, aiming to develop industrial environmental technologies for olivine applications, was divided in four main tasks, with the following content :

TASK 1 : Exploration of dunite / olivine bodies and mineral processing.
The main objective of this parf of the project was to locate the most promising dunite and harzburgite bodies in the ophioliate complexes in Northern Greece and to produce from them, through appropriate mineral processing techniques, olivine s and within the standard specifications required by the foundry industry (MgO > 48%, LOI < 1.5%, free SiO_2 < 1.0%).

TASK 2 : Industrial application of olivine as a foundry sand.
The main objective was to produce several cast if ems with the use of Greek olivine sand as moulding material. Several types of steel grades and cast iron were costed, under fully industrial conditions and the performance of the Greek "olivine" sand was examined in comparison with typical silica sand and Norwegian olivine sand.

TASK 3 : Environmental application of dunite / olivine.
The purpose of this parf of the project was to further more develop and optimize the neutralization process of industrial waste acids by olivine / dunite, a process which was invented and patented by one of the partners (Geochem Bv). The subsequent step was the improvement of the separation of the neutralized reaction mixture into valuable by-products (silica gel, inert mineral residue and residual Mg-salt solution). The texture of silica gel is very important for the various applications. An important target was to study the reaction parameters which influence the formation and the texture of the silica:

TASK 4 : Techno-economical assesment.
The objectives of this part of the project were to define the optimum production procedures, to determine the investment and operational costs and to examine the market possibilities of the Greek "olivine" product.

B.1 EXPLORATION OF DUNITE / OLIVINE BODIES AND MINERAL PROCESSING

cl. Geological exploration

This project part was divided into four (4) research areas :

1. Regional scale geological exploration of approximately 300 km of dunites / harzburgites in order to locate the most promising of-them for detailed follow-up prospecting.

2. Detailed exploration in selected ultramafic bodies including reserve estimation Particular attention was given to the open-cast mining activities (magnesite - chromite)

3 . Dunite / harzburgite process selection including pilot plant :.tale trials.

4 . Pilot - scale calcination tests of mine tailing and dunite in o der to obtain olivine sand meeting the requirements of the foundry -industry.

The Institutive of Geology and Mineral Exploration (IGME) was responsible for carrying out the subtasks 1,2,3, and MIRTEC for 4. ·

The field work started with the collection of 120 samples which covered the Western Chalkidiki ophiolites occurances [see fig 1). These samples were s objected. to mineralogical, mineral chemical and whole-rock analyses and the results obtained revealed dunites / harzburgites ranging from massive, unserpentinize types to strongly deformed and completely serpentinized ones.
This information combined with crushing tests, grain size distribution and inital fractional qualities, qualified the open-pits of Vavdos and Gerakini mines, the dunite bodies hosting the Vourinos chromite deposits and the South Vavdos and Galarinos areas, as potential olivine targets for follow-up exploration. At the same time large areas (Triadi, Gomati, Nigrita; Nea Roda) were discarded from further studies.

The regional scale geological exploration was followed by detailed exploration of the selected areas : Agia Anna and Loucovitis open pits of Vavdos are i, the South Vavdos area, the northwestern part of Gerakini mine, the Galarinos area and the broad area of the ", Vourinos ophiolite units. The follow-up exploration activities included mapping of the selected areas, sampling with regard to the mapping of ihe selected olivine prospects and analytical work in terms of mineralogical and whole-roc<" chemical investigation.
Bulk sampling of totally 4 samples, weighting about ? tonne each, was performed to serve the process selection and pilot plant tests. The four samples, two fresh dunite and two moderately serpentinized dunite, were taken from potential sites o Gerakini and Vavdos mines.
A second, more extended, bulk sampling was undertaken for the p reparation of foundry-sand fraction to carry out the industrial scale foundry application testing. Three samples were collected, representing the following qualities : Vavdos dunite {25 onnes), Vavdos harzburgite [12 tonnes) and Gerakini dunite (55 tonnes).

From the regional scale-and follow-up geological exploration the following results were drawn': ·

The Agia Anna dunites and harzburgites and particularly those from the ***main*** *dunite* ***zone*** *have MgO content ranging from* 46.9 *to 48.7 wt% and* LO. *I content 1.6-4.3 wt%.* ***A substantial*** *,amount* ***of*** *this* ***LO.*** *I. is* ***due*** *to the magnesite veinlets. In the Agia* ***Anna*** *pit- walls dunites and harzburgites* ***occur as very*** *large blocks (e.g. 20 tones each):* ***Based on the*** *macroscopically characteristicvs, selective exploitation might results in* ***l0*** *w* ***LO.*** *I. content* ***{e.g.*** *1.5-2 wt %) dunites* ***and*** *at* ***the*** *some time "fine impurities" such as* ***serpentine,*** *magnesite* ***and*** *soil will be* ***avoided***
Dunite ***and*** *harzburgite* ***reserves are*** *large* ***.2.-*** *and 7 million tones respectively) in* ***the*** *Agia* ***Anna open pit and if additional reserves*** *are needed, then the* ***south ward and north word*** *extension* ***of*** *this* ***zone*** *must be explored by means of shallo* ***w*** *(10* ***-15*** *meters) drills. The Louco vitis, Gerakini* ***and*** *south Vavdos areas are the next most promising targets for fresh dunites* ***-*** *harzburgites in* ***deeper*** *levels.*

The Rizo and Voidolakkos chromite districts seem to have large amounts of dunite and harzurgite comparable to those of the Agia Anna open pit.

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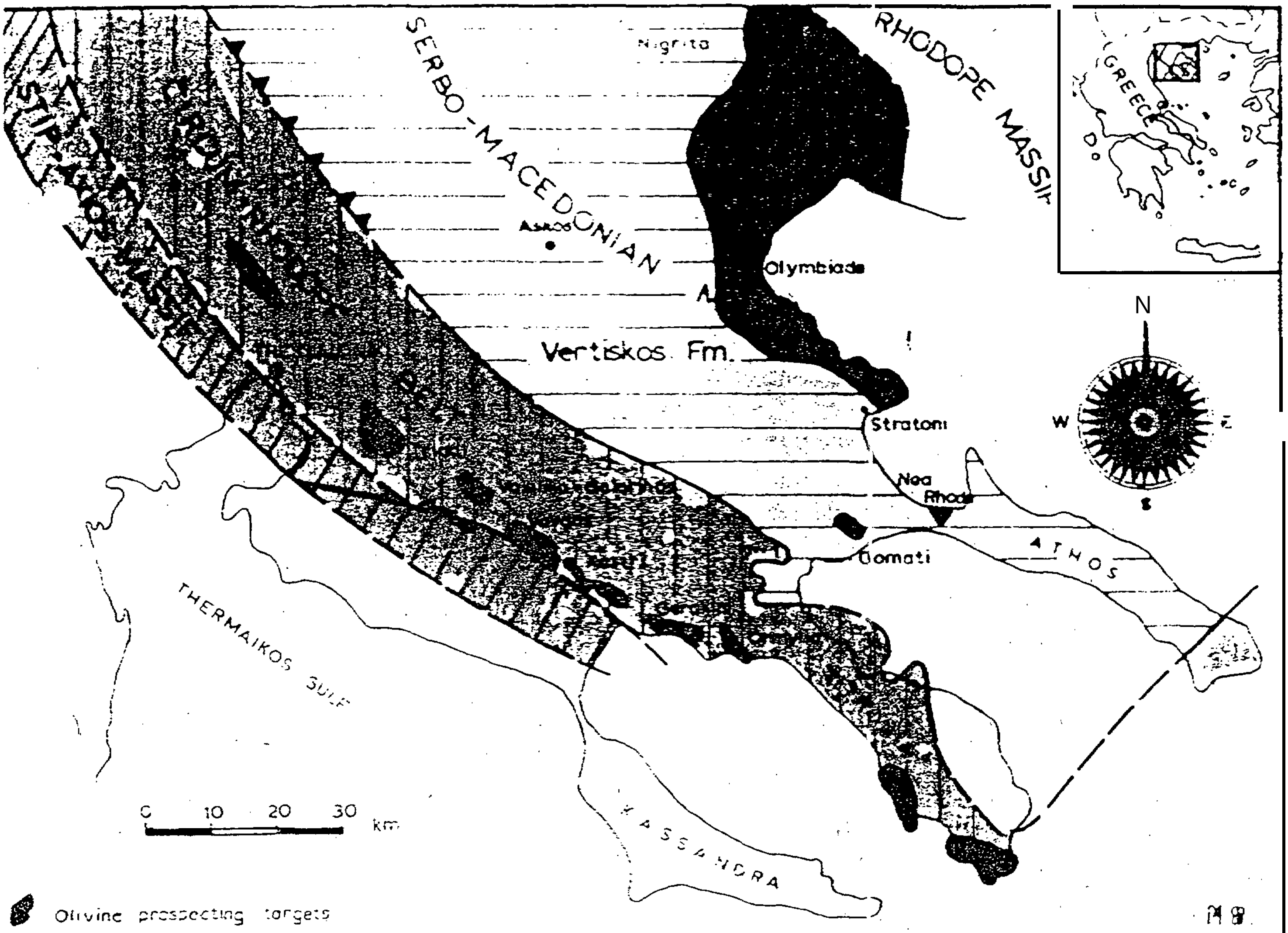


Fig. 1 Simplified structural sketch map of the Chalkidiki peninsula. Ophiolites are shown in black [illegible]

b. Mineral processing

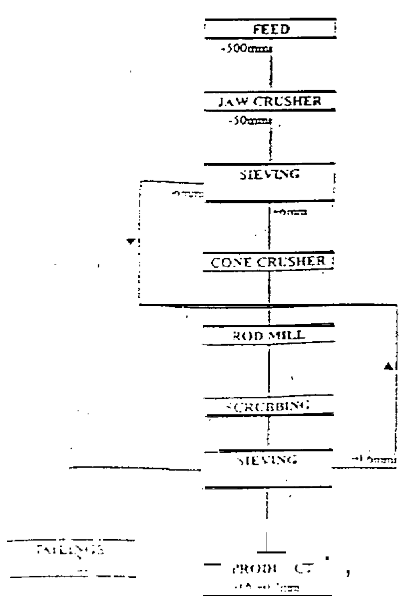
The scope of ihe mineral processing was to reveal the optimum conditions for the production of a product suitable for foundry applications. Such a product should have an MgO content > 48%, an L.O.I. content < 1,5% and a grain size of -0,6 mm + 0,21 mm. From the products' evaluation, it was concluded that, the samples originating from Vavdos give better results as far as the MgO and L.O.]. contents of the target products (foundry applications) are concerned. The work performed included grindability test work in laboratory scale and crushing, grinding, scrubbing and sieving in pilot plant scale. Four [4) bulk samples were used as the feed for these tests, in order to prepare adequate quantities of the appropriate grain size for preliminary foundry tests. Three (3) bulk samples were also prepared for the systematic foundry tests.
From the overall work, it was realised that it is possible to produce a group of samples with MgO and L.O.I. contents very close to the required. specifications for the production of foundry sand without beneficiation or/aria calcination and also a second group of samples for which these methods are necessary in order to achieve the required characteristics.

Magnetic and gravimetric separation tests were performed in samples which did not meet the required specifications Magnetic separation failed to improve the quality of the "olivine" products. Gravimetric separation improved the quality of the final product by reducing the LOI content by up to 2% and by increasing the MgO content by uc to 1.5%.

According to the results of all the above mentione testwork the following flowsheet for "olivine" processing is proposed (see fig 21.

Primary and secondary crushing (jaw and cone crushers), grinding (rod' mill), scrubbing and screening (wet). If grinding is applied in a closed circuit, the final product [0.6' + 0.2 mm) could represent approximately 60% of the feed. If the material is derived from Agia Anna, Vavdos area, ihe MgO content will be around 48% and the LOI content will be lower than 1% in the case of harzburgiyte ond below 2% in the case of dunite.

Fig. 2 PRELIMINARY PROPOSED FLOWSHEET for "OLIVINE" PROCESSING



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c . **Calcination tests**

Calcination is amplied to "olivine" sources with LOI content above 4 %, where gravimetric separation is not sufficient to produce foundry sand within the req uired specifications. This is for example the case of the tailings from the chromite beneficiation plant in Vourinos, where we have a product grinded to -200 μm, with LOI content around 6%.
Through laboratory and pilot scale experimental work it was revecled that calcination can reduce the LOI content of highly serpentinised dunited to below 1 % levels and subsequently increase the MgO content. The optimam calcining temperature is in the range of 8000-1 000°C and the reaction time 15-20 mins.
Three bulk samples from Vourinos, Vavdos (B-3) and Gerakini (Γ-3) areas were subjected 10 calcination and the derived calcined products were used for the foundry trials. The chemical analyses of the products before and after calcination are given in Table 1.

	Sample from Vourinos		B3		Γ - 3	
	before calcination	after calcination	before calcination	after calcination	before calcination	after calcination
MgO	43.6	48.1	48.00	50.6	42.9	46.6
SiO2	'39.9	37.4	40.30	38.6	40.0	40.6
Cr2O3	2.?	2.85	0.50	0.50	0.70	0.70
A1203	0.7	0.65	0.15	0.35	0.55	0.55
Fe203	6.6	6.86	7.65	8.21	8.25	9.00
CaO	1.4	0.50	0.35	G.50	0.60	0.80
LOI	6,3	0.75	2.10	0	5.3	0

Table 1 : Qualities of foundry sands used as moulding materials

From the above results it was revealed that through calcination even the most serpentinized dunites met the required quality for foundry applications.

B.2 INDUSTRIAL APPLICATION OF OLIVINE AS A FOUNDRY SAND

In this part of the work dunites and harzburgites originated from the most promising areas of Chalkidiki and Vourinos districts were examined as moulding materials. The experimental work was carried out under fully industrial conditions at BMTE installations, and it was supplemented by MIRTEC 8A.

The research work was divided in two parts

1. Characterization of the different Greek "olivine" sands
2. Casting trials

a. Characterization of the moulding sands

Seven different kinds of moulding materials were examined within the present research programme, as they are presented in table 2.

No	QUALITY OF SAND	CODE	LO I%"	MgO%
1	Harzburgite from Vavdos area	B-4	0.9	46.4
2	Dunite from Vavdos area	B-3	1.96	47.0
3	Calcined dunite from Vavdos area	B-3c	0.0	50.6
4	Calcined dunite from Gerakini area	Γ-3c	0.0	46.6
5	Harzburgite from Vourinos area	s-1	1.2	47.0
6	Norwegian olivine	N-1	0.38	49.6
7	Typical silica sand	x-1	--	--

Table 2 : Qualities of foundry sands used as moulding materials

The first five products are typical Greek "olivine" sands originated from the most promising target areas. These dunites / harzburgites were subjected to mineral processing in order to obtain the required grain size, (-0.6 + 0.21 mm). Two of the above Greek productes were also calcined in order to' reduce their LOI content.
Typical silica sand and Norwegian olivine sand were also examined in parallel to the Greek products, for comparison reasons.

All the above moulding materials were subjected to the following analyses, according to the applied standard procedures, in order to characterize their qualify as foundry materials.

- Determination of the moisture
- Determination of the LOI contents
- Sand sieve analysis
- Permeability test
- Compression test
- Refractoriness under load

From the abo ve testing if was concluded that the quality of the Greek olivine products is comparable to the quality of the other typical products in the mar ket /silica sand, Nor wegian sand). Silica sand showed a higher value of refractoriness under load, compared to all "olivine" products. The grain size of the Greek products was coarser than that of the silica and Nor wegian olivine sand.

b. Casting Experiments

Different kinds of steel, and iron grades were tested using the previously mentioned moulding materi als. The experimentation used the following qualities :

Manganese steels : Type : GS-120 (12% Mn 1.5% Cr)
Stainless steels : Types : GX40 CrNiSi 25 12
GX40 CrNiSi 25 20
GX40 CrNiSi 18/8

Low alloy steels : Types : GS 42 CrMo4
GS 30 NiCrMo 6.5.6

Carbon steels : Types : GS-60
GS-45
GS-52

Grey cast iron : Type : GG-25

Write cost iron : Type : MAXICHROME (C:2.3%, Cr:1 8%) "

Two different procedures were followed in preparing the moulds.

"DWVET" PROCEDUCE: Foundry sand was mixed with bentonite (7%-14%), water (3%-7%) and albertine (1 %1.
When silica sand was used as moulding material the surface of the moulds were covered with a special magnesium coat called Mo_4CO 330.

"DRY" PROCEDURE : Found sand was mixed with phenolic resin (2%-3.5%) and catalysts (0.470-0.6701

The following parameters were studied during the experimental procedure :

- Kind of foundry sand
- Moulding procedure _
- Casting temperature

The results of different moulding and costing conditions were evaluated based on the surface quality of the produced castings. Surface quality was determine by two ways.
. By visual comparative inspection of the received castings' surface
. By measurement of roughness of the castings

Following the above, the respective results are as follows :

Casting of manganese steels

- *In general, **Greek** olivine **sand produced better results** than the typical **silica sand** and **Nor**wegian olivine sand, even in cases in which the MgO co[?] of the olivine sand was **10**wer than 48% and the **!** OI content greater than **1.5%:** = non-calcine**d** dunite from **Agio** Annal.*
- *Olivine **sand** gives better results with "dry" moulding procedure than **with,. "wet'** moulding **procedure.** The later is **cheeper** than the first. Consequently the choise between **the Iwo depends on** the prevailing **factors of** the case at hand, **e.g.** cost or quality.*
- *Increasing the MgO content ' and reducing **!** OI **content,** which can be obtained by **,** calcination, improves the **p**erformance of the casting process*
- *The casting temperature is **one** of the most important factor which influances the castings' quality. For manganese steels 1500°C seems to be the optimum temperature*

Stainless - steels, low allo v steels, carbon steels

- In general, silica sand gave better results compared to Greek "olivine" sand, specially in the case of application of the "wet" procedure. Bentonite seems not to be the , appropriate binding material for "oh-vi-@- send at high casting temperatures.
- When the "dry" procedure was applied with "olivine" sand, the qualify. of the received , castings was comperable to that of the silica sand castings.
- The Jo wer the LOI content of the "olivine" sand the better the quality of the cast items.

Cast irons

- Greek "olivine" sends performed absolutely satisfactory in the casting of cast irons, eventhough the "wet" procedure was applied. It seems that bentonite cooperates satisfactory with olivine, sand, at low temperatures, although higher quantities are required compared to /hose required with silica sand.

B.3 OPTIMIZATION OF THE OLIVINE PROCESS

The olivine process is being developed as a new process to neutralize industrial waste acids. Compared to conventional methods of treatment of waste acids, the olivine process bears the advantage that apart from the neutralization of acids it produces valuable by-products and generates no new waste streams. The reaction of olivine and acid is exothermic and produces, after 'starting-up, enough heat to sustain itself.
The most important by-products are :

- precipitated silica: applicable as filler in a wide range of products
- magnetic ferrites: e.g. for heavy-media separation
- magnesium sulphate: e.g. for fertilizers or raw material for MgO and H_2SO_4

The improvement of the olivine process for the neutralization of waste acids was airned at optimizing the neutralization reaction, mainly in terms of reaction rate, in combination with the production of good quality by-products. Furthermore it was of great importance to study the effects of scaling up in order to facilitate a pilot plant design.
In figure 3 a simplified process flow diagram of the olivine process is presented. A concise overview of the research carried out on the reaction sections is presented below.

1. Optimization of the neutralization reaction
The parameters that control the neutralization reaction were divided into three groups.

a.) First of all the effect of the olivine properties was investigated. One of 'the most important factors controlling olivine dissolution in acidic solutions was found to be the degree of agitation applied in the reaction vessel. If the ground olivine is not agitated, a firm layer of precipitated silica is formed on the surface of the grains, resulting in a diffusion 'controlled reaction rate. In stirred experiments the reaction rate is determined by surface" reactions, and thus proportional to the available olivine surface area. The use of a finer olivine fraction or an excess amount of olivine will result in an increased neutralization rate.
Apart from the purity of the ground olivine rock, the degree of serpentinization, microstructure of the olivine crystals and the iron content of the olivine are important parameters, determining the reactivity of the ground olivine.
The reactivity of pure olivine grains, separated from two Greek olivine samples (from the Vavdos and Geraikini magnesite mines) and a Norwegian sample (A.S. Olivine) was compared. The results are displayed in Figure 4, it can be clearly seen that the Greek olivine samples react faster. The higher neutralization rate was explained by higher serpentinization degrees and iron contents of the Greek samples.

b.) Second the possibility to neutralize various acids was investigated.
It was shown that with the olivine process a wide range of acids can be treated, it is however necessary to make specific adaptations to the process for every type of waste acid. For this project four acid types have been used: technical grade sulphuric "acid (25%), sulphuric waste acid with anorganic contaminants from a titanium-dioxide plant and two waste acids with organic contaminants (hydrochloric and sulphuric acid). Main conclusions are: the neutralization rate of the TiO_2 waste acid is comparable to technical grade sulphuric acid, the neutralization rate of both waste acids with organic contaminants is however higher.

Furthermore it was revealed that the specific surface areas of the silicas produced from the sulphuric waste acids' are comparable to those made with technical grade sulphuric acid, the silica from the waste hydrochloric acid, however, has a lower specific surface area.

c.) Several reactor types have been tested. ranging' from stirred batch reactors (0.5 to 10 liter) and fixed bed reactors to autoclaves. It turned out that the mixture of olivine and acid has to be stirred in order to prevent cementation of the olivine grains and to maintain a high react ion rate. The use of fixed bed' reactors is therefore not successfull. The tests carried out in the autoclaves 'showed that it is possible to carry out the neutralization reaction at temperatures up to 200 "C, as long as the 'reaction mixture is stirred well. Higher reaction temperatures have the advantage, of an increased neutralization rate. The first scaling up step from 1 to 10 litre stirred bed reactors was succesfull, similar results were obtained under the same reaction conditions.

2. Silica separation & silica washing

The silica produced by the olivine process can be used for a wide range of applications, the purity of the silica depends on the type of application. Since the silica cake still contains a considerable amount of magnesium salts after the first filtration it is generally necessary to wash the cake. The filtration and washing **procedure** hove to be optimized, depending on the type of silica produced and it's application.'

The use of a chamber filter press, operated under 5 bar nitrogen pressure, 'proved to be ideal for the filtration and subsequent washing of the silica.

3. Processing of the magnesium-salt rest solution

The magnesium-salt rest solution can be used **as a** raw material for several products, for these purposes the rest solution has to be clean. Depending on the type of acid used, different strategies have to be followed to produce clean solutions. For this project the processing of the rest solutions from the technical sulphuric acid and the titaniumdioxide waste acid was studied in detail.

a.) The technical sulphuric acid rest solution contains apart from Fe some Ni and Mn. The best way to separate these metals from the solution is to partly oxidize the iron. and precipitate a magnetic ferrite. The advantage of precipitating a magnetic ferrite is not only the fact that it is easily separated from the solution (by magnetic separation), but the ferrite itself might also have an economic value. Numerous combinations of oxidants [like air, nitrate and H_2O_2) and pH-buffers (to neutralize the H^+ formed during precipitation) have been tested. The best method was found to be the use of $Mg(NO_3)_2$ as oxidant and MgO as pH buffer. The use of these reactants clearly has the advantage that no new ions are introduced in the solution, spar? from that the synthesis time is short compared to air oxidation.

b.) The rest solution from the titaniumdioxide waste acid contains beside Fe, Ni and Mn considerable amounts of Ti, Al, V and Cr. This last group of metals can be easily, separated by increasing the pH to about 4.5, followed by a filtration. The remaining solution can subsequently be processed as the rest solution from technical sulphuric acid neutralizations.

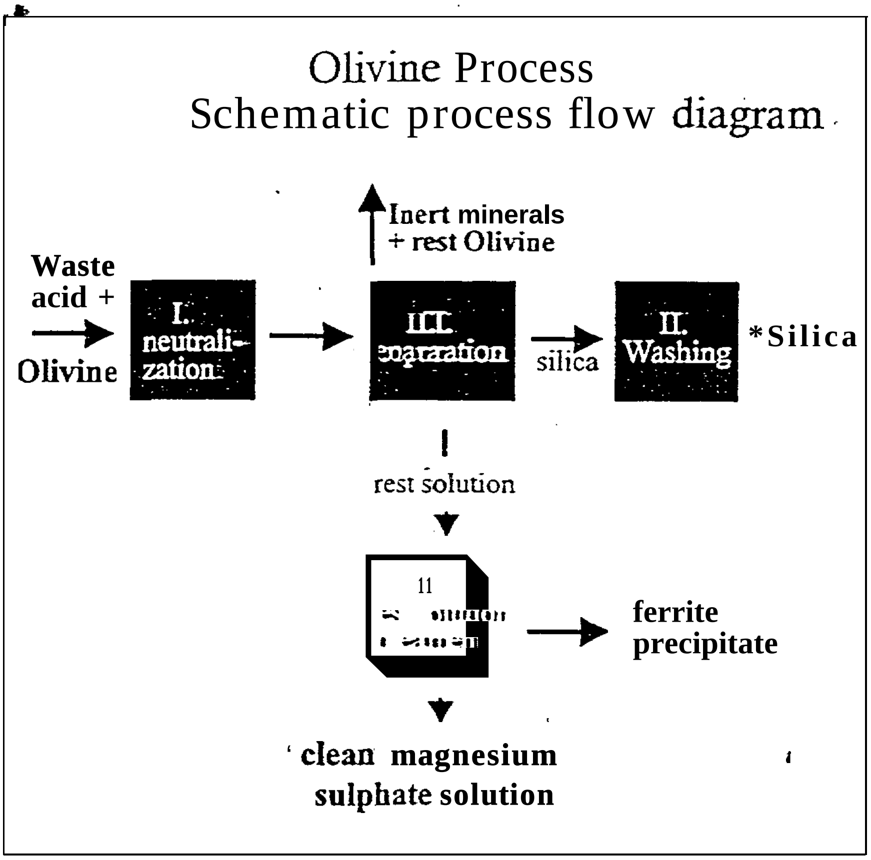


Figure 3 . Set er iatic **process flow diagram**

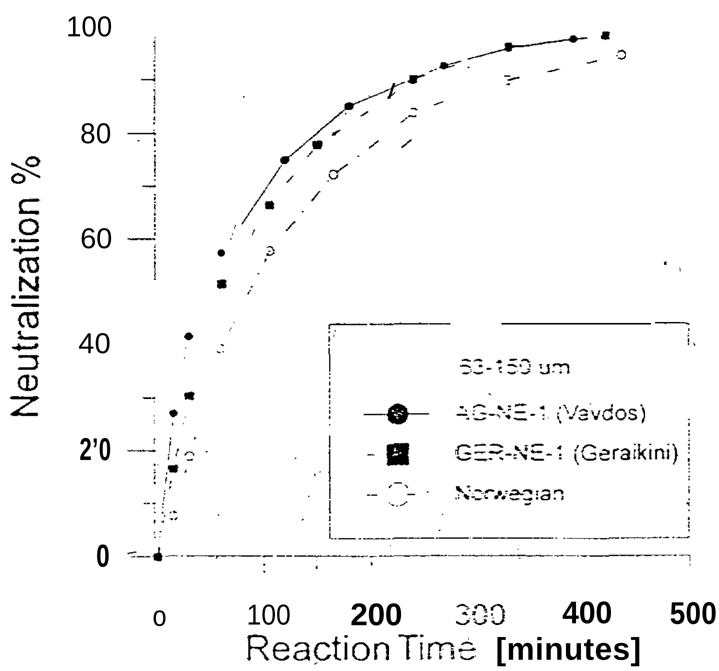


Figure 4 . Neutralization % vs reaction time fo Norwegian and Greek Olivines and two grainsize fractions

B.4 CONDITIONING AND CHARACTERIZATION OF SILICAGEL - "". PRODUCED BY THE NEUTRALIZATION PROCESS '

The neutralization of sulphuric acid using olivine yields a pure, white silica, " which can be, used in many different applications. The reaction can be described as

$$(Mg,Fe)_2SiO_4 + 2H_2SO_4 \longrightarrow 2(Mg,Fe)^{2+} + 2\ SO_4^{2-} + Si(OH)_4$$

Three molar sulphuric acid is used together with stoiciometric amounts of olivine.
The produced monomers of silica will polymerize in the acid and salt environment and produce a colloidal solution of clustered silica particles in a highly concentrated magnesium-sulphate solution.
The most important aim of this part of the research project was, to study the texture of the silica [specific surface area, particle size, pore size distribute ons] in relation with the dissolution reaction parameters. Important parameters are the temperature and the grainsize of the olivine.
Shortly, a high temperature yields a high reaction rate as do fine olivine particles.
Experiments were performed at 30,-50, 70 and 90°C. Three ! grainsize fractions have been used:
Z< 90µm [very . fine], 90<Z<425µm (fine) and 425<Z.C100@m (coarse). Some experiments at 150 and 200°C have been done at the VerTech laboratories in Apeldoorn, the Netherlands.
Typical values of the specific surface areas of the olivine silicas are presented in table 3

Conditions	BET S.A. (t-t? /g)	M? S.A. (n?/g)	EXT S.A. (n#/g)
30 °C/fine olivine	157	27	130,
30°C/coarse olivine	217	90	127
70°C/very fine	428	**92**	**336**
70°C/fine	415	"144 "'	271
70°C/coarse	335	107	2 2 8
.150°C/ coarse	426	101	3.25

Table 3: Some *typical textural data* ***of*** *olivine silica.*

From these data it is clear that the higher the temperature or the smaller the grainsize of the olivine, the higher the specific surface area. This points towards a proces where a fast dissolution reaction gives a high specific surface area. In the third column the micropore specific surface area is presented. The micropores seem to be more abundant in silicas produced at higher temperatures.
During the reaction, samples of the colloidal solution have been taken from the reaction mixture. These samples have been separated from the magnesium sulphate, washed, dried. The, texture was analysed by nitrogen physisorption. These procedures do not influence the texture. The drying temperature does not exceed 200°C.
Fig 5 gives *a* typical linear increase of the particle size. of the silica during most of the reactions. In some cases a constant particle size is observed as shown in fig 6.

Fig 5. evolution of particle size of olivine silica (D2)
pH range 43.5-0. T=70°C coarse olivine

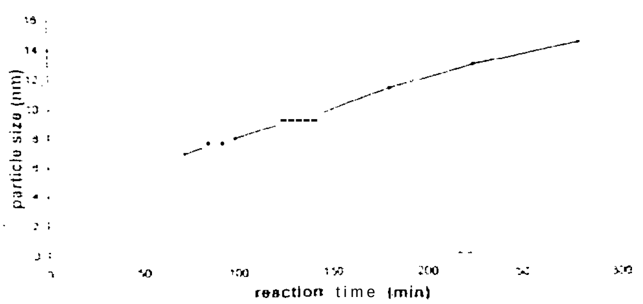
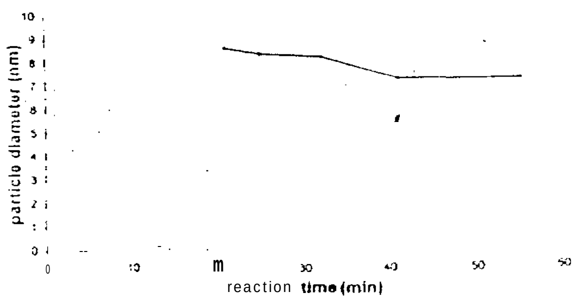


Fig 6 evolution of particle size of olivine silica (D3)
pH range -0.1-0.3. T=70°C very fine olivine



The important difference between these two experiments is the reaction rate caused by the olivine grainsize. The results can be explained by a "crystallization/growth" model. When olivine is dissolving, the monomers enter the solution and a monomer concentration is created. At a certain moment this monomer concentration reaches nucleation saturation and the silica particles nucleate. When the product ion of monomers is very quick, the monomer concentration renains higher than the nucleation concentration and constantly nucleation takes place. When the monomers are produced slower, using **a** coarser olivine the concentration decrease: under the nucleation concentration but remains above the supersaturation. Then the silica particles will grow and the specific surface area will decrease.
The growth rates of the silica at different temperatures have been established and are listed in table 4.

Temperature ("c)	**growth rate (nm/min)**
30	0.0006
50	0.004
70	0.01
90	0.02

Table 2: Grew:,% ***rates*** *of silica particles*

Using these growth rates it is possible to prepare a "tailor" made silica with a specific surface area between 100 and 400 m^2/g.
For some applications we need a lower specific surface area. Then a hydrothermal treatment can be given. It is possible to decrease the specific surface area down to approximatly 60m^2/g.

The olivine silica has been tested in various applications. A preliminary test as additive to rubber proved succesfull. Tests in concrete and refractories showed that the specifc surface area of 150m^2/g was too high.
The production of a nickel on silica catalyst was succesfull, the catalyst showed the same activity as a nickel catalyst based on commercial silica.
The preparation of synthetic clay minerals based on olivine silica was also very succesfull.

C. TECHNO-ECONOMICAL ASSESSMENT

The techno-economical assessment included the following topics :

- Study of the olivine consumption in Northern and Southern Europe
- Marketing possibilities of the end products derived from the "olivine" process
- Cost estimation of Greek oliivine sand production for use in four dry applications
- Budget estimates for' "olivine" neutralization according to Vertech's processing

D. CONCLUSIONS

From the experimental work and the techno-economical assesment carried out within the present research programme, the following conclusion were derived :

- In Northern Hellas, there exist estanded deposits 'of "olivine" sources of comparable quality to other "olivine" sources in market
- Since the above deposits are connected to existing manganese and chromite mining activities, from which they derive as by-products, there are not charged with quarrying costs
- The cost estimation for the production of Greek "olivine" sand is comperatively low compared to the FOB prices of the other "olivine" products in market
- Since the cost of olivine sand remains nigher that the cost of silica sand the trade perspective of the Greek product will depend on "
  - growing demand of olivine in terms of increasing c resumption and enhancing development in new application areas
  - national environmental measures restricting the use of quartz in the metalliferous sector due to healthy concerns
- The use of Greek "olivine" sand in stead of silica sand, as foundry material is advantageous in the case of casting manganese steels and cosi irons, where the casting temperature is relatively low. In the case of casting other steel grades (high alloy low alloy, carbon steels) silica sand gave better results. The practice showed that the use of low cost binders, like bentonite, does not give to the olivine sand good performance during casting.
- The "olivine" process which has" been invented to neutralize industrial waste acids with olivine is an environmentally and economically attractive procedure. The process can be further developed as new industrial method to produce precipitated silica, synthetic clays, synthetic zeolites and/or high purity magnesium-suiphate products.
- Two important applications of the produced silica are possible. It can be used as a high-quality product ot replace silicas which are presently on the market. In this case the silica would have to be quite pure and will have to nave the required specifications further research is needed to develop this spinoff of the project. The same applies for the use of this silica to produce synthetic clays and zeolites. Another application is the use of silica in concrete or cement. Applied research in conjuction with end-users is needed to produce the specific qualities needed by these industries.

  If the price of the silica, magnesium-sulphate solution and/o- magnetic ferrites can be realized the process can provide o positive cash flow, which in 'the case of a waste treatment process is quite unique. If no price for the end-prod Jets can be made the costs of neutralization per tonne of acid are estimated to be fl. 80/tonne which is still competitive with prices which are being paid by the industry for the treatment of their waste acids (fl. 100/tonne or higher).