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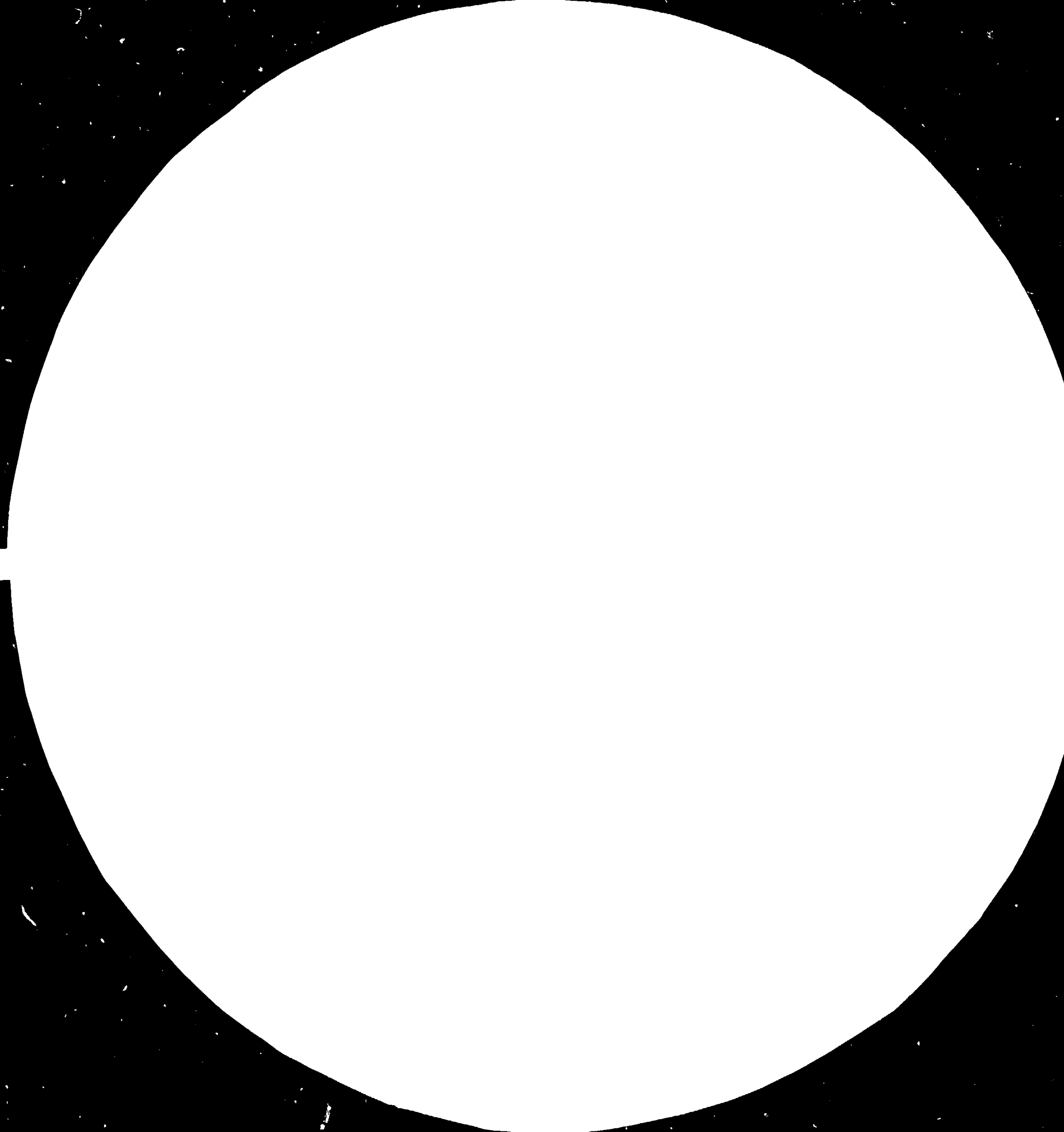

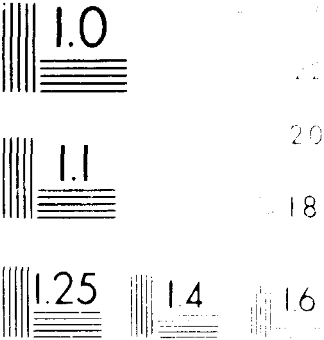
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INDUSTRIAL UTILIZATION OF BENTONITE

IN VITINA COMMUNE

DP/YUG/80/004

YUGOSLAVIA

Terminal report

Prepared for the Government of Yugoslavia
by the United Nations Industrial Development Organization,
acting as executing agency for the United Nations Development Programme

Based on the work of Károly Szepesi, expert in bentonite activation

United Nations Industrial Development Organization

Vienna

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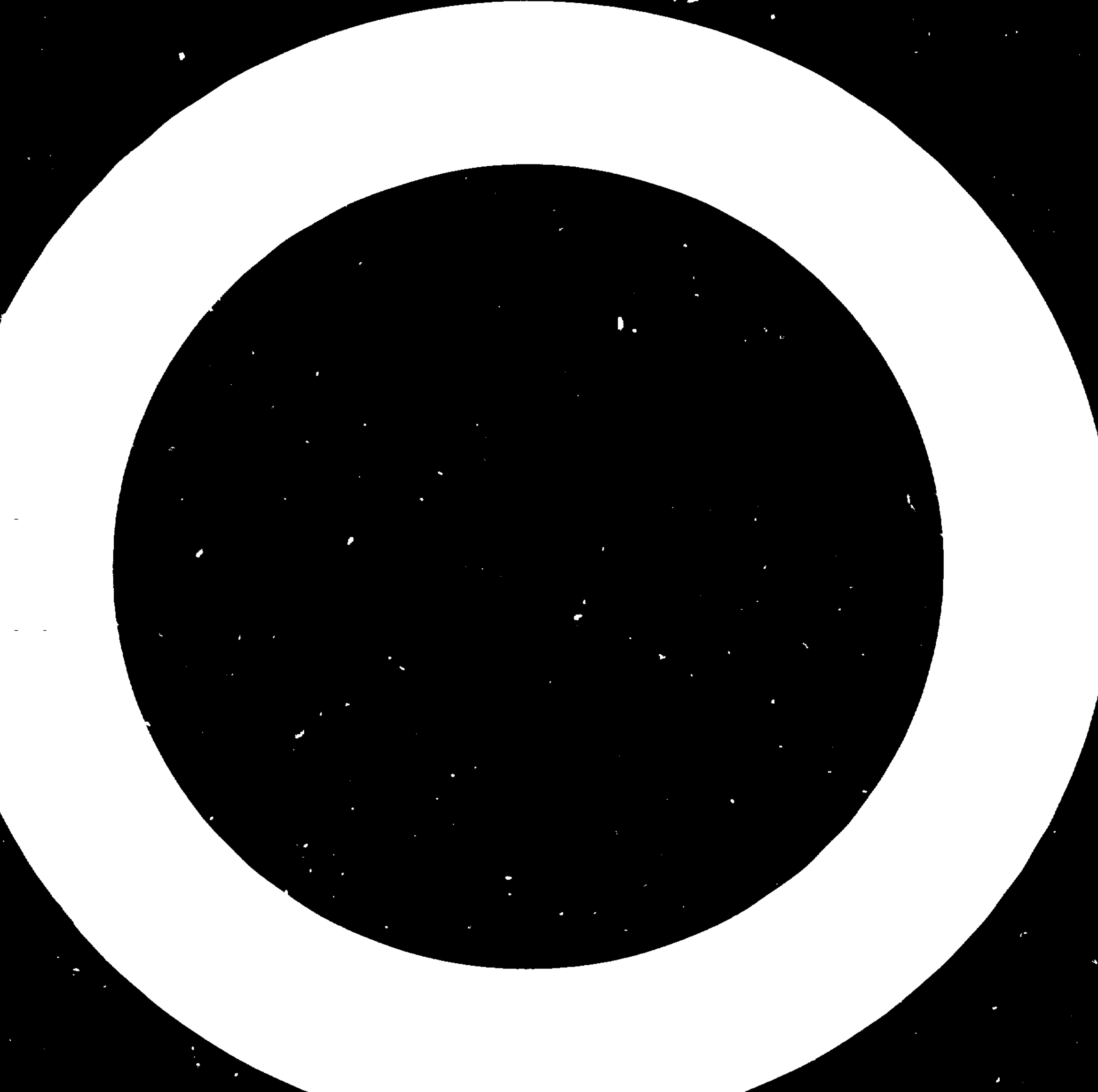
ABSTRACT

The United Nations Development Programme (UNDP) project "Industrial utilization of bentonite in Kosovska Vitina Commune" (DP/YUG/80/004) implemented from 2 July 1980 to 22 August 1981 - formerly UNIDO/SIS project "Expert in bentonite" (SI/YUG/79/801) covering the period from 12 May to 15 November 1979 - had as its main objective the definition of optimum techno-economic solution for industrial utilization of bentonite. Other objectives were the determination of appropriate technologies for the production of metal salt, particularly of potassium salt, from leucite rock, as well as the production of building materials based on pumice-stone or on ceramicite.

The expert accomplished the tasks listed in the Project Document and solved problems that were beyond project objectives. He also trained technical personnel.



CONTENTS

INTRODUCTION

Within the framework of the United Nations Development Programme (UNDP) project "Industrial utilization of bentonite in Vitina Commune" (DP/YUG/80/004) an expert was sent by UNIDO to Kosovska Vitina, Yugoslavia, to find an optimum techno-economic solution for the industrial utilization of bentonite. The project, which was implemented from 2 July to 22 August 1981, was formerly a UNIDO/SIS project entitled "Expert in bentonite" (SI/YUG/79/801) covering the period from 12 May to 15 November 1979.

The objectives of the project were the evolvement of solutions for the industrial utilization of various minerals in the Vitina Commune, particularly of bentonite, leucite, pumice-stone and ceramicite.

The immediate objectives were the definition of optimum techno-economic solution for industrial utilization of bentonite; the determination of appropriate technologies for the production of metal salt, particularly of potassium salt, from leucite rock, as well as for the production of building materials based on pumice-stone or on ceramicite.

In addition to the regular duties within the framework of the project, the expert was also expected to assist the Kosovo authorities in a faster valorization of metallic and non-metallic raw materials (see annex).

In connection with the tasks, objectives and activities under the present programme several technical and special reports were written. The technical reports are summarized in the following paragraphs.

The "Preliminary report on the bentonites in Kosovska Vitina, Yugoslavia" (SI/YUG/801/11-01/32.1.B) was submitted to UNDP, Belgrade and to UNIDO in 1979. It gives background information and basic technical information on the bentonite deposits in the region of Kosovska Vitina, Yugoslavia and the results of various investigations of bentonites. The Gusica and Jerli Sadovine bentonites are more accessible to activation (upgrading) by conventional methods, which would make them suitable to industrial and civil engineering application.

The second technical report, which was submitted to UNDP, Belgrade and UNIDO in 1981, deals with the utilization of bentonites in the Kosovska Vitina region under the UNIDO/SIS Project (SI/YUG/79/81) and covers the period from 2 July 1980 to 15 April 1981. It gives the quantity/quality data of the bentonite deposits in the Kosovo region, at Gusica, Jerli Sadovine and Karačevo, together with their genetic and geological conditions. It also gives the new methods of testing and analysis introduced by the expert, the theory of bentonite activation and the technology thereof, as well as the results of laboratory tests and analyses performed. The report also describes the activities related to the contemplated large-scale tests in England, i.e. the analyses of approximately 15 tonnes of raw material prepared earlier by the company for the large-scale tests.

Following a request of the Bentokos Vitina Enterprise the expert prepared a confidential report in Serbo-Croatian in 1981, giving a complete and detailed description of the technology of bentonite activation.

A detailed report was prepared on the large-scale bentonite activation tests in England, including the work performed at NEI Engineering Derby Co., and at Greven and Fawset Co., Wakefield, England.

The expert collaborated with Zoran Dimitrijević, chief engineer, in preparing a report on the large-scale tests performed at six large Yugoslav foundries using the bentonite samples produced and packaged during the test in England. These tests were made by the Institut za Hemiju, Tehnologiju i Metalurgiju (IHTM) of the Centar za Livarstvo, Belgrade. The report is also available at the Bentokos Vitina Enterprise, for which these tests were made.

FINDINGS AND CONCLUSIONS

A. Findings

Bentonite activation tests carried out in England

The performance and results of the large-scale bentonite activation tests in England are summarized in the following paragraphs.

The Bentokos Vitina Enterprise has prepared about 16 tonnes of raw bentonite, mostly in 1980. The bentonite samples were obtained from the Gusica deposit, from shafts sunk 8 to 16 metres deep below the surface. Difficulties were encountered on account of the relatively high position of the ground-water table. These bentonite samples contained about 25 to 30 per cent of calcium carbonate ($CaCO_3$), whereas the layers explored before were of better quality but had only 8 to 16 per cent of calcium carbonate. The high calcium carbonate content was accompanied by a lower montmorillonite, thus active agent content in the raw bentonite. Since the high ground-water table was an obstacle to the retrieval of any better-quality bentonite from the deeper layers, and since the enterprise wanted to ascertain the quality of activated bentonite produced by the method from the deposit, the expert raised no objections as to the quality of the raw bentonite prepared for the large-scale tests.

The large-scale bentonite activation tests were carried out in England in October 1980, partly in Wakefield (mixing and extruder test, but without steam-heating) and partly in Derby (drying and grinding process, further packaging) as had been planned, except for the drying process. The proper drying equipment (Buetner-type), which had been proposed, was not available so that drying could not always ensure the desirable 8 to 12 per cent residual moisture content in the bentonite. In spite of these difficulties, the results of the large-scale tests were satisfactory.

The analyses of the activated bentonite gave the following results:

(a) Mineralogical composition. The bentonite contained up to 40 per cent montmorillonite at 25 to 30 per cent calcium carbonate since the bentonite originated from the top, contaminated layer;

(b) Foundry properties. According to the IHTM report form strength properties are rather satisfactory. Plasticity (Shotter index: 90 per cent) and gas permeability are excellent. The foundry results are satisfactory;

(c) Rheological properties investigated at the Faculty of Technology and Metallurgy, Belgrade. In 6 per cent dispersion viscosity is 11 to 16 centipoise (11-16 mPa.s), filtration loss (API) is 15.6 to 18 ml.

These results are satisfactory, but if the rather poor quality of the raw material is taken into consideration, one could say that they are very good.

It should be noted here that the IHTM report also analyses the economic aspects of the bentonite activation process. According to the results obtained the process is economically feasible.

By the proper selective extraction of the raw Kosovo bentonite, or by combining different qualities, a raw material of a desirable quality can be obtained.

Leucite processing

In the area of the Vitina Commune (Visoce) an important leucite rock formation exists and can be extracted by surface operations. The volume and quality conditions and the geology of the formation have been explored earlier, especially by Predrag Ristić, professor at the Tuzla University, in his PhD thesis. The Visoce leucite deposit consists of 6 to 7 million tonnes of "monolith" type and 60 to 70 million tonnes of "breccia" type leucite. The average chemical composition of the "monolith" type is (per cent): SiO_2, 49.06; Al_2O_3, 14.52; Fe_2O_3, 7.01; TiO_2, 1.24; CaO, 8.59; MgO, 3.94; MnO, 2.42; K_2O, 8.48; Na_2O, 0.63.

According to tests carried out in the Netherlands the leucite contains additionally considerable amounts of rare metals, such as rubidium, samarium and europium. The recent analyses in Yugoslavia failed, however, to substantiate the presence of these rare elements.

In view of the high K_2O content and since all potassium fertilizer has to be imported it was considered desirable to develop an economical technology for extracting the potassium from the leucite in the form of a salt that could be used as potassium fertilizer.

Since the early 1960s, several attempts have been made in this direction, so that literature on the subject is available in Yugoslavia. The papers by V.G. Logomerac, Faculty of Technology, Zagreb University, are of special interest. About 50 per cent of the potassium present in the leucite can be dissolved by sulphuric acid at 80° to 90°C, but only together with the aluminium oxide. Subsequent crystallization results, however, invariably in the development of a double salt, namely potassium aluminium sulphate. To extract the potassium sulphate from it Logomerac suggested a pyrogenic separation method, which unfortunately proved uneconomical. Although the research efforts at several Yugoslav institutes took about 10 years, they produced negative results and the efforts were discontinued. The UNIDO expert was therefore assigned the task of developing a method of processing that is more economical and technologically simpler.

In solving the problem the expert relied on his extensive experience gained with similar problems; that is, the extraction of various metal oxides bound in silicates, using inorganic acids, to produce the desired salts. He gave advice on both the theoretical and technological aspects of such processes. The expert had in the past developed methods for extracting by acid treatment Al_2O_3, MgO, K_2O, CuO, NiO, as well as oxides of other metals, such as Zn, Cr and Pb, from silicate bonds.

The expert described this method in a lecture at the Bentokos Vitina Enterprise and demonstrated the process to the staff of the enterprise. Although the laboratory facilities available did not permit a complete quantitative analysis to be made, the results showed that leucite is processed solely by inorganic acid in a simple way and that the main components, such as $Al(OH)_3$, magnetite and amorphous SiO_2, can be separated from it with the simultaneous recovery of potassium, ammonium and calcium fertilizer salts with the desirable nitrate content.

The new technology suggested by the expert for processing the leucite consists of grinding the rock to < 70 micrometre fineness and adding 0.8 to 1.5 per cent by weight of a suitable activator. The activator is an inexpensive salt that has the required chemical composition. The slurry is heated for one to two hours at 80° to 100°C in an inorganic acid (HCl, H_2SO_4, HNO_3) by which all metal oxides are dissolved into salts. The filtrate residue contains SiO_2 and magnetite alone. From the filtrate residue the magnetite can be easily removed by means of a magnetic separator, or the silicic acid can be extracted with a NaOH at fairly low temperature (100° to 120°C) as water-glass. If nitric acid is used, all salts in the filtrate consist of nitrates, from which the aluminium can be separated with ammonium hydroxide in the usual way as $Al(OH)_3$, which can be separated from the other salts by filtration and is thus available as a valuable product for further use.

A more detailed demonstration was organized at the Agrochemical Research Institute, Novi Sad. Árpád Sel, engineer of the Novi Sad Fertilizer Factory (IHP PRAHOVO BAS.B.R.O. Agrohem, Novi Sad), was interested in the process and offered financial help in realizing this demonstration. The first demonstration conducted by the expert was repeated subsequently several times by Árpád Sel on samples taken earlier by an expert committee under the guidance of Predrag Ristić from the surface layers of the Kosovo leucite deposit. These samples contained less K_2O than the average and had the following chemical composition:

	Monolith leucite (Percentage)	Leucite breccia (Percentage)
SiO_2	48.90	47.42
TiO_2	1.98	1.78
Al_2O_3	14.96	14.74
Fe_2O_3	6.19	7.86
FeO	3.42	2.28
MnO	0.21	0.11
MgO	2.63	3.20
CaO	9.10	8.15
K_2O	6.79	6.09
Na_2O	1.29	1.43

From both leucite types 86 per cent K_2O could be dissolved by the cold process and 93 per cent during about 90 minutes at 80° to 85°C. This was accompanied by about 85 to 90 per cent of Al_2O_3.

The above results, the whole process with its economic aspects, and the product output were reported on by Árpád Sel at a company meeting in the presence of the expert and the Kosovo professionals. On the basis of the estimated average composition of the leucite the report gives the following product balance and the flow diagram of production:

Starting volume	200 000 t leucite per year
Energy demand	183 262 m^3 natural gas
Chemical demand	105 000 t NH_3 (gas)
	360 000 t HNO_3
Products	81 000 t colloidal amorphous silicic acid SiO_2
	12 000 t magnetite ($Fe_2O_3.FeO$)
	37 000 t $Al(OH)_3$
	33 000 t KNO_3
	44 000 t $Ca(NO_3)_2$
	57 000 t NH_4NO_3

The rest consists of the nitrates of TiO_2 and minor quantities of salts, including those of the rare metals.

The report was approved by the meeting and the director of the Novi Sad factory, Milan Samardžija, engineer, said that he would try to procure finances for compiling a feasibility report on the process. The further necessary steps will be agreed upon depending on the results thereof.

Building materials (ceramicite, tuff (pumice) block)

An Augsburg firm (Federal Republic of Germany) had submitted an offer to the Bentokos Vitina Enterprise, concerning the production of light-weight concrete aggregate from the overburden of one of the bentonite deposits (Jerli Sadovine). It was claimed to consist mainly of illite clays, which could be processed to expanded clay material, suitable for use with cement bonding as light-weight aggregate for light-weight concrete building blocks. The analytical results on the samples submitted failed to substantiate this claim, i.e. both the mineral and the chemical composition of the material proved unsuitable for this purpose. Therefore, the addition of materials of higher Al_2O_3 and Fe_2O_3 content and even of bauxite was recommended. Although this would encounter no substantial obstacles, since low-grade, cheap (diasporic, böhmitic) bauxites abound in the Kosovo district, the expert raised objections to the production and use as building material of the light-weight concrete blocks made with ceramicite aggregates. The objection was that these blocks were expensive to produce, that they required major investments and that the durability of such materials was poor, which means that such blocks would loose strength and deform in time. Earlier studies by the expert show that if the fines (sand fraction) of the light-weight aggregate consist of ceramicite, these combine owing to their possolanic properties by a hydrothermal chemical reaction not only with the free lime of the concrete, but also with the cement mineral hydrates, thus reducing the strength of the concrete. The pH of the concrete decreases successively and since carbonic acid H_2CO_3 is a stronger acid than silicic acid H_2SiO_3, the CO_2 content of the atmosphere causes rapid decomposition, thus accelerating concrete deterioration.

The use of sand instead of ceramicite as the fine fraction would remedy the situation in many instances, but would at the same time raise the costs of the blocks and increase the unit weight of the concrete. This approach cannot therefore be put into practice.

The expert found that the particular bentonite deposit contained no illite clay, but that it was composed of minor amounts of montmorillonite and higher proportions of volcanic tuff (pumice). The pumice had pronounced pozzolanic properties and so did the overburden and the surface layers of high $CaCO_3$ content covering the bentonite deposit at Gusica.

In combination with the required amount of $Ca(OH)_2$ both materials can be processed by simple brickmaking technology to hydraulically bonded, even large, hollow blocks. These would have densities of 1,250 to 1,600 kg/m^3 and strengths ranging from 100 to 200 kgf/cm^2 (10-20 MPa). Moreover, the materials would be highly durable. The expert demonstrated the correctness of these claims in the laboratory.

The building blocks can be made of the pumice by an identical process, but with higher proportions of lime than in the case of the overburden.

The exploratory boreholes were sunk, and the geological, mineralogical and chemical investigations on the foregoing tuff deposit at Vitina were made, by the Geological Survey, Belgrade, for the General Janković Cement Factory, Kosovo. The factory intended to use the ground tuff as additive to its Portland cement. The amound foreseen was from 20 to 25 per cent. The report on these investigations was not completed during the assignment period of the expert and repeated requests resulted only in a single tuff sample for the analyses mentioned above.

B. Conclusions

The expert accomplished the tasks listed in the Project Document and solved problems beyond project objectives. Also, he trained technical personnel, mostly young and inexperienced, in performing the analyses introduced by him. Considerable difficulties were encountered because of the very modest laboratory facilities.

Although all the problems contained in the programme were solved substantially, in a way fully consistent with the project objectives, their industrial realization will depend on the availability of funds.

Annex

TASKS BEYOND THE PROJECT OBJECTIVES

The expert also performed tasks that were not part of the project objectives.

Improvement of the technology at the Priština brick factory

Following an invitation by Musa Balanca, director of the brick factory, the expert conducted an investigation into the causes of the large proportion of rejects at the brick factory, with the aim of finding the remedial measures and improving production performance. The problems were due not only to the high proportion of rejects, but also to the relatively long time required for drying and burning.

The expert found that the raw material, at least as presently excavated, was not based on illite clay mineral, as indicated by the analysis of the Research Institute at Niš. The six samples analysed by the expert showed the raw material to consist of 40 to 45 per cent montmorillonite and of 50 to 60 per cent volcanic tuff. The successive layers are in various stages of dispersion and their rheological properties differ considerably. To homogenize these differences the expert suggested the addition of 2 per cent of lime hydrate and the passing of raw mixture twice through the extruder press. The 2 per cent $Ca(OH)_2$ could be replaced by the fly ash containing high amounts of CaO (40 per cent) from the Obilić thermal power station situated nearby (8 to 10 km). The ash should be added at the rate of 5 to 10 per cent.

The method suggested proved highly effective. The hollow brick specimens made at the laboratory could be dried without damage at 100°C (rapid drying), the specimens could be fired directly to 600° to 700°C and the temperature could be increased to 850°C (rapid burning). On the basis of these results, the management of the factory took the necessary steps to introduce and initiate technological trials on the new method for autumn 1981. Moreover, the expert introduced laboratory tests and analyses related to the new technology. For these he equipped a corresponding laboratory and trained the personnel to perform these laboratory analyses.

Analysis of the lignite deposit at Kosovo

A firm from Milan submitted a proposal for an improved method to gasify the Kosovo lignite, but the preliminary tests failed to produce the desired result. The expert was therefore invited to examine the lignite deposit of Kosovo from this aspect.

The analyses showed that the coal classified as lignite was not composed of the constituents corresponding to lignite, but rather of a mixture of marsh algae and pollens. For this reason the coal contained rather high proportions of $CaCO_3$, which could be traced back to the biological activity of the algae.

The algae are known to assimilate as plants CO_2, rather than oxygen, and to obtain oxygen from the dissolved $Ca(HCO)_2$ content of the lake, releasing $CaCO_3$ in very fine distribution. This $CaCO_3$ surrounds the decaying and carbonizing complex of high organic humic acid content. Removal of this $CaCO_3$, e.g. by flotation, would influence benficially the calorific value and the suitability to gasification of the coal.

Nickel ore analysis

The expert was invited to examine two different nickel ores for the possibility of gaining nickel salt by simple acid dissolving.

The expert found the nickel ore of 6 to 6.5 per cent nickel content to be essentially a bentonite, in which the montmorillonite mineral contained the nickel oxide, replacing Al_2O_3 in the octahedral lattice. The other ore was halloysite mineral, which contained about 3 per cent of nickel in silicate bond. Applying the method used also in the case of the leucite, the expert demonstrated successfully the recovery of nickel from both ores in the form of nickel sulphate.

Production of water-glass

Instead of the conventional manufacturing technology for water-glass or "white soot", involving the pyrogenic processing of quartz and soda, the expert produced economically pure colloidal silicic acid from a number of different silicates, using the method described in connection with leucite processing. By dissolving the silicic acid simply in NaOH at temperatures between 90° and 120°C water-glass can be obtained.