PROCESSING TECHNOLOGY ASPECT OF SILICATE AND OXIDE RAW MATERIALS*

By

R. KRSTULOVIČ

Tehnolosk i Fakultet, Split, Yugoslavia Laboratorij za Anorgansku Technologiju

Received November 11, 1980

Presented by Prof. Dr. I. SZEBÉNYI

Introduction

In the present state of the world's industry, special attention must be paid on plans and objectives of development of each industry. Furthermore, it is essential to know how to implement these plans of development, as they are closely connected to the economic development of the given country.

The essential elements of development control are: scientific implementation of objectives, planning, carrying out developmental activities with a system control mechanism.

Plans of development can be short- or long-range, and they often contain solutions to a number of problems. So in the chemical, as in any other industry, the following possibilities and objectives of development have to be kept in mind:

— safeguarding of raw material and energetic sources;
— guaranteed permanent increase in production and optimal utilization of the above sources;
— provision of the necessary equipment for the technological process, as well as of the necessary material reserves and consumption;
— permanent implementation of plans of development, as well as training and recycling of the personnel;
— efficient integration of the progressive and developed industry into the international division of labour and its adaptation for cooperation in the technical and technological processes of development.

Planning of objectives of development is rather difficult in small countries, where unexpected problems may create disequilibrium likely to restrict their implementation, especially in the chemical industry. Small countries cannot keep up with the bigger ones because technological revolution achievements affect several fields particularly in the case of developments in production in the chemical industry.

* Presented at the 3rd Conference of Chemical Technology Departments of Socialist Countries, on 14-th April, 1980 in Balatonfüred.

Studies undertaken so far on elements and objectives of development programs in industrial technology, showed that the chemical industry, just as any other one, may be studied and analyzed as a separate system, dependent on a number of internal and external factors. The qualitative and quantitative properties of these factors restrict possibilities of development in every industry.

The internal factors are: raw materials, energy, technology, personnel and funds. External factors comprise: domestic and foreign market, the economic and social system.

The raw material being one of the most important internal factors in every industry, it is necessary to examine the conditions of optimum use of the raw material and to realize the objectives of the process of development. When speaking about raw materials, the following must be taken into account:

- the need for industrial products increases in close connection with the increase in applicability and the increase in population.
  This applies to the developing countries in particular.
- The raw material sources are soon exhausted.
- Every country must try to base the development of her industry on the maximal processing of her raw materials.

It is necessary to intensify research with a view to gradually replace imported raw materials by domestic ones, and at the same time to develop the application of alternative sources of raw materials.

This report on our research on Dalmatian sources of raw materials [1] is intented to point out the importance of these sources for future generations. The study of the quality and technological applicability of raw material is becoming more important, even imperative in Yugoslavia, when planning new factories and plants or reconstructions, or widening the range of products.

In the Socialist Republic of Croatia, and its region Dalmatia, extensive investigations have been carried out to detect potential sources of raw materials, to examine their quality and quantity.

Not so long ago these investigations were considered to be an additional financial burden on the industry. As a matter of fact, good quality silicate and oxide raw materials could always be found in sufficient quantities for the production of cement, brick, lime and bauxite. The existing plans of development, however, provide for increasing capacities and raw factories and plants setting up. Thus, in cement industry the production was significantly increased by having installed two rotary kilns of 1200 tons of clinker per day and one of approximately 3200 tons per day. Furthermore, construction of an alumina factory of about 320 000 tons per year in Obrovac imposed beside knowing the quality of the actually utilized raw material estimation of the quantity and quality of reserves. To this aim extensive physical-chemical, geological-mining and technological research was started in Dalmatia.

Knowledge of the quality of raw material reserves and other important details permits to foresee the position and development of Dalmatian cement industry. Today's programs of bauxite research lack this anticipation, and it is necessary to develop them more intensively.

Dalmatia abounds in silicate, oxide and carbonate minerals such as silica sand, quartz sediments, various clays, shale limestone and dolomite but their technological applicability has not been examined in detail excepted limestone, so that they have only a potential value.

This paper deals with the above raw materials from the aspect of physical-chemical properties and possibilities of technological processing scope of our scientific and applied research work for several years. A methodology has been developed for testing the quality of various raw materials, influencing factors of the technological process got established in order to use the raw material more rationally in factories, and to compress and process the raw materials to obtain more profitable products.

From this aspect the most difficult problems are to find proper testing methods and to assign raw materials for certain technology. There are no relevant general rules and instructions except the geological examination of raw materials. The empirical system of raw material examination integrate various procedures and methods. Results of various methods are seen to be interdependent and the data of mineralogical-petrographic examinations match the physical-chemical and technological properties of some raw materials. These principles are valid in industrial examination as well.

Raw materials in Dalmatia: origin, properties and industrial applicability

Marls, clayey-limey marls, limestones

The marls were first used in cement production about 100 years ago in the Split region, when the first cement factories were built here. But a more extensive and systematic research into the state and quality of these raw materials did not start sooner than 50 years ago. At that time, construction of the modern cement factories in the Solin area began [2]. This may be taken to be the first capacity increase, followed by several reconstructions. It should be pointed out that the strong development of the cement industry near Split was closely linked to deposits of high-grade raw material. At first the exploitation went smoothly, as the deposits were in the immediate vicinity of the factories, involving little transport costs. Unfortunately they are now exhausted, and the cement factories have problems to acquire good quality marls.

In Dalmatian marl deposites several sedimental layers can be distinguished. The layers belong to three zones. The about 100 m thick middle zone contains 76.5 to 77.0% of $CaCO_3$. It is the ideal raw material to be burnt to clinker for cement production, to be called "cement-clay" below. The zone below the zone of exploitation may be 30 m thick, its main components are limestones with 80 to 98% $CaCO_3$. In the zone overlying the cement-clay there are marls with sandstones and limestones; the content of $CaCO_3$ averages at 60%. This zone does not suit exploitation.

According to the qualitative X-ray analysis the sediment components making up cement-clay consist of two basic components ideally mixed: $CaCO_3$ in the form of calcite, and clay composed of quartz, illite, montmorillonite, muscovite, kaolinite and chlorite. In the other two zones, the components proved to be the same as in the cement clay, but in other rations with more (above 77%), and less than 76% of $CaCO_3$ called "high" and "low" component, respectively.

The "low" component contains an excess of clay minerals, so that much limestone should be added in order to obtain good quality cement.

The cement industry has been using cement-clay for a long time with no additions or corrections for burning clinker.

The exploitation of good quality raw material, i.e. cement-clay is almost at an end. One cannot anticipate this parameter of the raw material composition that cannot be kept within permitted boundaries.

Therefore, the problems in connection with the raw materials have to be studied by the concerned industries as well as by scientific institutes in particular the quality and composition of the raw materials.

Initially the raw material quality was maintained simply by selectively sieving the raw material. The cement-clay was fed into vertical kilns in bigger and smaller lumps. The experience has shown that a high proposition of small lumps impairs not only the quality of clinker but the consumption of fuel as well. This directed the attention on the influence of cement-clay grading and composition on the chemical and mechanical properties of clinker thus, of cement. Bigger lumps of cement-clay were separated into two sizes by sieving in an inclined rotating drum with 20 mm sieve mesh. In this way, both grading and quality of cement-clay was improved.

The analysis showed the "small" lumps passing through the sieve to contain less than 76% of $CaCO_3$. They were discarded as dirt, while the bigger lumps, remaining on the sieve, had a satisfactory carbonate content (76.5%) yielding good quality clinker. Properties of raw materials and clinkers obtained by this method have been collected in Table 1.

Recent extensive geological and mineralogical examinations have proven, however, the cement-clay deposits, the natural raw material of clinker to be almost exhausted. Thus the time has come to start exploiting sediment layers thought previously to be inadequate and uneconomical as raw material, but which can be found in large quantities. These sediments are marls, marly limestones, clayey marls, etc. They all contain a low percentage of $CaCO_3$, are

Table 1

The influence of selective sieving on cement quality

Mechanical properties of cement type 250	without % preparation	with % preparation
Grinding fineness		
4900 mesh/cm^2	10.3	9.7
Bending strength (kp/cm^2)		
3 days	30.4	37.0
28 days	43.9	52.0
Compressive strength (kp/cm^2)		
3 days	154	244
28 days	230	311

mixed with other layers and overlying the cement-clay. Their average content of $CaCO_3$ is about 72%. The layers with a prevailing content of limey marls contain approximately 88% of $CaCO_3$.

In short, the problems raised by poor quality raw material, as well as the increased demand for cement production, have led to investments of up-to-date cement factories near the existing ones. Two new factories were built with rotary kilns of 1200 ton capacity of clinker per day, and one with a kiln of 3200 tons per day. A systematic scientific research of raw material and technologies has been started. In new working conditions, special attention is paid to raw material preparation, since the work with one-component raw material now turned to work with raw material powder of two or more components.

Our research has thus been directed to the preparation, composition and quality, of the raw material powder determination of its reactivity optimum operating conditions for kilns and quality of the clinker produced. Other research concerned to obtain cements of special properties and types from the same raw material, such as high early strength or sulfate-resistant cement; experiments were made on the Dalmatian white clay to obtain white cement. The reactivity of the raw material powder was tested in various cement factories. Although roughly the same initial raw materials were used, the reactivity varied. Except when pyrite was added to the raw material, the reactivity proved to be significantly affected by previous preparation of the raw material (grinding, homogenization, admixtures etc.) Table 2 and Figure 1 show the test results.

From the aspect of cement production at a constant quality, correct, about constant composition of the raw material powder, has to be ensured especially in large production units. Let us take the rotary kiln of 3200 tons

Table 2

Formation of clinker minerals at different temperatures determined by X-ray analysis

Sample No	4			6			7		
Burning temp. °C	1250 °C	1250 °C	1340 °C	1150 °C	1250 °C	1400 °C	1150 °C	1250 °C	1400 °C
Burning time (min)	20	30	20	30	30	30	20	30	30
C_3S	48%	52%	60%		55%	65%			60%
$-C_2S$	32%	23%	18%		20%	15%			15%
C_3A	1%	18%	18%	Begininng of formation of clinker constituents	2%	8%	Beginning of formation of clinker constituents formation of $-C_2S$'		8%
F.f. phase	17%	1%	1%		7%	4%			6%
Free CaO	1%				1.5%				

Sample No	5			1			8		
Burning temp. °C	1150 °C	1250 °C	1400 °C	1150 °C	1250 °C	1400 °C	1400 °C	1250 °C	1400 °C
Burning time (min)	20	20	20	10, 20, 30	20	20	30	30	30
C_3S			70%		38%	45%	47%	45%	60%
$-C_2S$	Beginning of formation of clinker constituents		10%	Beginning of formation of clinker constituents	38%	40%	38%	30%	20%
C_3A			6%		4%	3%	7%	12%	5%
AF-phase			6%		8%	8%	6%	8%	7%

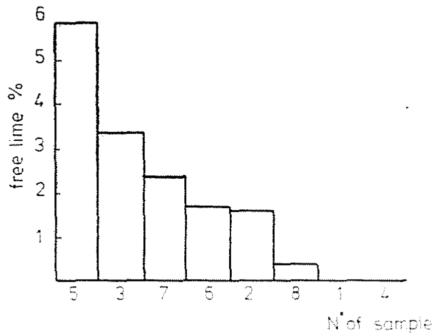

Fig. 1. Reactivity of different cement-clay samples. Samples 1—3 are raw materials for experimental burning; sample 4 is the raw material with Fe_2O_3 addition for experimental burning; samples 5—8 are raw materials used in various cement factories for clinker production

of clinker per day as an example. The technological process in this kiln is not imaginable without an automatic laboratory for controlling preparation and quality of raw material. This type of laboratory system periodically (usually every hour) controls the raw material supply. In the classical way, it would take approximately 24 hours. That is about 1000 tons of clinker produced might fall short of the composition requirements. In kilns of large capacities, quick interventions are needed especially when more-component raw materials are concerned, stressing the importance of an X-ray fluorescent analyzer. This laboratory control system can ensure constant composition of raw materials and clinkers. A complete analysis of all the data required together with calculations takes about two minutes. A further advantage of this system is that it can correct the raw material powder composition by itself if some irregularities occur. So far, the raw material has still been manually composed, but soon a computer system will control the complete process of preparation, analysis and correction of raw material (Table 3). Complete automation of this process will pursuit to feed raw material of constant quality in to the kiln, and to increase the clinker production.

We have also studied the influence of the composition of the raw material on the consumption of crude oil, using a Humboldt kiln of 350 tons of clinker per day. During several days the raw material composition was measured together with the crude oil consumption. Fig. 2 shows the crude oil consumption in dependence on the degree of saturation of the raw material and clinker. Systematic measurements appeared to be necessary in order to obtain quantitative correlations for deducing general rules. On the other hand, this type of examination is useful if one wants to affect oil consumption by using special techniques of starting fire, depending on the properties of the liquid fuel used.

Table 3

X-ray fluorescent analysis of high and low components of raw materials and of raw material powder by automatic laboratory method of raw material preparation and control

No	$CaCO_3$ %	SiO_2 %	Al_2O_3 %	FeO_2 %	CaO %	LSF %	SM	AM
1	80.28	12.3	2.4	1.3	45.1	118.3	3.3	1.8
2	86.69	7.2	2.1	1.0	48.7	211.2	2.4	2.2
3	81.57	11.17	2.59	1.23	45.7	130.0	2.8	2.1
4	95.05	3.3	1.0	0.6	53.4	497.3	2.2	1.7
5	92.74	4.8	1.0	0.6	52.1	346.2	2.9	2.7
A	66.75	17.8	5.4	2.4	37.5	65.3	2.3	2.3
B	70.67	17.7	3.9	1.8	39.7	72.2	3.1	2.2
C	68.35	17.6	5.3	2.4	38.4	67.6	2.3	2.2
D	74.58	13.8	3.8	1.6	41.9	95.4	2.5	2.4
F	72.27	08.0	3.6	1.8	40.6	72.9	3.3	2.0

Calculated moduli of various raw mixes by automatic laboratory method

raw mix	LSF %	SM	AM
1 + A	100.89	2.90	1.99
2 + B	101.39	2.89	2.15
3 + C	101.08	2.59	2.16
4 + D	107.55	2.54	2.34
5 + E	93.28	3.31	1.94

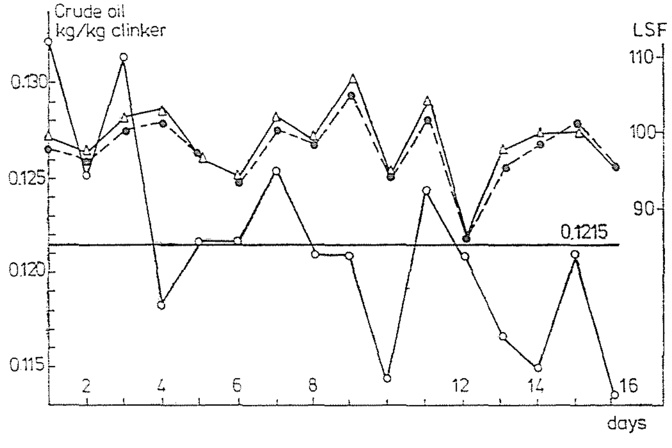

Fig. 2. Crude oil consumption ps. lime saturation (LSF) of raw material and clinker

Clays, tuff, shale

Large quantities of clay are found in Dalmatia. Its composition varies with the location of deposit. Further geological examinations are necessary to find its real technological application. The clay deposits detected so far have been used in the natural state for brick production or as a composite with the addition of bauxite and other substances. In this way the quality of the basic clay mass is improved to suit rough ceramic products.

Tuff has been used so far only as an admixture to cement. It is little used in cement industry because of its high degree of humidity and variable chemical composition.

Also various types of shale are found in several locations. These raw materials, as well as clays and tuff, have been examined in laboratory and pilot plant test with a view to producing expanded aggregates. These raw materials proved to suit lightweight expanded aggregates either in themselves or admixed with other substances. The fractions of the expanded samples were tested as lightweight concrete aggregates. Raw materials and resulting lightweight expanded aggregates have been compiled in Table 4. These raw materials should be further examined geologically, in order to find their industrial applications.

Table 4

Properties of expanded samples and concrete

Properties	Type	Fractions (mm)			
Density of expanded aggregate samples (kp/dm^3)		0—5	5—10	10—20	20—30
	1	1.10	0.87	0.61	0.51
	2	0.89	0.60	0.54	0.52
Density of concrete made with different fraction and to ratios (kp/dm^3)	1	1.07—1.82			
	2	1.37—1.72			
Bending and compressive strength (kp/cm^2)		compressive strength		bending strength	
		7 days	28 days	28 days	
	1	280	315	33.4	
	2	230	270	27.5	

Quartzites, limestones, dolomites

Quartz sediments are found in large quantities in a number of locations. So far they have been used in cement industry and as a melter in production of ferro-alloys (Fe—Cr, Fe—Mn) being of satisfactory quality for these purposes. They have been examined in order to improve chemical composition of quartz in preparation. As a matter of fact, a better quality quartz is needed for the ferro-alloy industry to realize its plan of producing 45 to 75% Fe—Si. The technology of ferro-chrome and ferro-manganese production can use only quartz particles above 20 mm, these have been separated by sieving in the field. During decades a great quantity of quartz below 20 mm has accumulated, as a waste material, affecting the cost of quartz exploitation.

A systematical examination of other fractions for technological applications showed the discarded quartz to be of interest for a number of industries by virtue of its chemical composition and grading. Separation by water washed out clayey and humus substances, almost all of Al_2O_3, a great part of Fe_2O_3, and TiO_2 and Cr_2O_3 almost completely. The percentage of SiO_2 could be increased from 95% to 98% an excellent material for producing 75% Fe—Si. This method of separation increased the yield from 42% to 50%, with the lower boundary of the fraction maintained at 10 mm [3].

The limestones in Dalmatia are used for lime-kilning, to produce hydratized lime, a perfect building material. Not long ago it was processed to calcium carbide. Pure limestones will not be used in the cement industry for a long time. Therefore, other industrial technological applications have to be examined. They are very pure raw materials with a high content of $CaCO_3$, from 98.5 to 99.5%.

Dolomites of excellent quality are found in large quantities. Their chemical composition is theoretically ideal. So far they have little industrial application. Laboratory and pilot plant tests showed dolomites of high purity to replace limestones for sedimenting magnesium hydroxide $Mg(OH)_2$ from sea-water. The magnesium oxide burned at high temperature has shown a high degree of purity as well as other excellent physical characteristics. Table 5 shows the quality of these raw materials as well as of magnesium oxide obtained in laboratory.

Bauxites

During the last fifteen years large capacities for bauxite production were set up in Yugoslavia; they are all operating today. Therefore, ever larger quantities of good quality bauxite will be exploited, in fact, new factories will start working at full capacity. The bauxite industry is in a difficult position, since as the examinations confirm, the possibilities of natural ways of exploitation of good quality ore have been exhausted. Mining research costs for the bauxite industry increase day by day. The price of bauxite barely meets the costs of the normal process of production. Further problems are encountered in mining exploitation, since the bauxites lying deep under the surface are now to be exploited.

Table 5

Average composition of limestone, dolomite and magnesia from sea-water

Chem. comp.	Limestone	Dolomite	MgO CaO precip.	MgO CaOMgO precip.
Ignition loss	43.50	47.20		
CaO	55.70	30.55	1.3 — 0.5	1.6
MgO	0.40	22.31	98.60—99.20	94.2
SiO_2	0.35	0.02	0.30— 0.02	2.3
Al_2O_3	0.065	0.025	R_2O_3	0.30
Fe_2O_3	0.10	0.04	0.1—0.03	0.47
TiO_2		0.007	B_2O_3	
			0.60—0.05	
S	0.018	0.012		
P	0.005	0.005		
$Na_2O + K_2O$	0.12	0.105		

Table 6

The comparative results of determination of the mineral composition of bauxite

Mineral	RD %	GA %	$\Delta 1$	RP %	AR %	$\Delta 2$	RP %
Hydrargillite	21.40	20.09	2.69	15.27	20.89	0.51	2.38
Boehmite	43.60	42.26	1.34	3.07	41.96	1.36	3.12
Diaspore	0.00	—	—		—		
Kaolinite	3.20	2.96	0.24	7.50	2.96	0.24	7.50
Goethite	10.60	—		—	9.67	0.93	8.77
Hematite	15.60	—			15.49	0.11	0.71
Anatase	2.00	—			2.88	0.38	15.20
Rutile	0.50						
Calcite	1.10	0.88	0.22	20.00	0.88	0.22	20.00
Chemsorb. water	1.60	—			1.48	0.12	7.50

RD = X-ray method
GA = graphical-analytical method
AR = the alkalic digestion method
$\Delta 1$ = absolute difference
$\Delta 2$ = in relation to ΣRutile + Anatase
RP = relative error

The bauxites used in alumina processing normally contain approximately 8% of SiO_2. Although laboratory and pilot plant tests have been made to desilicize and enrich bauxite, but so far there is no method applicable in the alumina industry. Therefore, the bauxite quality has to be constantly checked for supplying the factories bauxite with tolerable SiO_2 content. Our research [4] was concerned with new methods for testing the chemical and mineralogical composition. Mineralogical bauxite composition is determined by chemical analysis consisting in the alkalic digestion of bauxite samples. In this way, a number of minerals in bauxite can be determined easily and relatively quickly. Table 6 confronts results obtained by this method and by X-ray analysis.

Our research work [5] has also dealt with the digestion kinetics of various types of bauxite, conditions of digestion in the technological process with regard to exploitation and other data, as required by up-to-date industries.

Discussion and conclusions

The development of every industry is controlled by the quality and quantity of raw materials available and other sources, factors of the development of the national economy.

The development factors are internal or external. One of the internal factors of importance is the raw material quality determining the possibilities of processing technology.

The research on silicate and oxide raw material occurring in Dalmatia involved technology aspects. Geological examinations underlie technological evaluation of applicability both of binders and of silicate materials.

Up-to-date cement production technology in Dalmatian cement factories was conditioned by extensive research on quantity and quality of the raw material. New investments were realized parallelly and other possibilities to modernize the technology had been recourse to, outdated plants were reconstructed.

In artifically processing the raw materials, the basic and most difficult problem was a good knowledge of properties of raw material components, in order to maintain constant clinker quality. The analyses on samples from raw material deposits, from pilot plant tests or representing daily mean compositions of clinker obtained from new kilns have shown significant differences in the quality of clinkers obtained from artificially processed or natural raw materials. Processing of raw material in the new plants merits a special interest. Very good results were obtained with the automatic laboratory system of control of preparation and quality of raw material, when standard raw material enters the kiln at set time intervals.

On the other hand, it is necessary to know not only the basic physical and chemical properties of the raw material but the affinity of the raw material powder to clinkerization as well. Reactivity data of the raw material are instructive for the technologist in using the new raw material quality and behaviour in the kiln. The raw material quality may influence the crude oil consumption and permits energy saving in clinker burning.

The examination of technological applicability of other silicate and oxide raw materials under laboratory and pilot plant conditions indicated their usefulness for future industries producing rough ceramics, wrapping glass fibres, volastonite, expanded lightweight aggregates, etc. The same applies to dolomites which could perspectively be used for producing dolomite lime or magnesia bricks.

Beside the raw materials for cement and the limestones also bauxites are very important stressing their technological examination and evaluation, bearing in mind the forthcoming poorer quality raw materials.

Technological examination of raw materials completed by geological and mining research, thus a systematic examination of raw materials offers a completer evaluation of the raw material deposits for some technology and its economic significance.

Summary

Effect of raw material properties on cement and alumina production technology is discussed. The relations between properties and utilization of dolomites, limestones, quartzites and clays are described. Different analytical methods for evaluating raw material properties and for fast production control are presented.

References

1. Krstulovič, R.—Urličić, M.—Pivčević, P.: Experimental research on Dalmatian nonmetal raw minerals for the purpose of technological processing. 5 Jug. simpozij o pripremi sirovina, Split 1975. Zbornik rada p. 7
2. Krstulovič, R.—Pivčević, P.: Experimental work aiming at the production of cements with low C3A content. Cement-br 4/1972 p. 189—197
3. Krstulovič, R.: Ispitivanje utroška mazuta u ovisnosti karakteristike sirovine za pečenje klinkera trinaesti znanstveno-stručni skup o Primjenskim instraživanjima do racionalne energetske potrošnje. Simpozij Yugoma '79 Cavtat 24/26 okt. 1979.
4. Krstulovič, R.—Perić, J.: The comparative chemical investigation of bauxite. 4th Congress of ICSOBA Vol. 1: Bauxites p. 449—466 Athens, Okt. 9—12 1978.
5. Krstulovič, R.—Perić, J.: Comparative experiments in bauxite digestion (paper at ICSOBA-AIM Conference Sept. 26—28, 1979 Cagliari).

dr. Ruža Krstulovič { Laboratorij za anorgansku technologiju Technoloski Fakultet 58 000 Split, Yugoslavia Testina 10.