



TOGETHER
for a sustainable future

OCCASION

This publication has been made available to the public on the occasion of the 50th anniversary of the United Nations Industrial Development Organisation.



TOGETHER
for a sustainable future

DISCLAIMER

This document has been produced without formal United Nations editing. The designations employed and the presentation of the material in this document do not imply the expression of any opinion whatsoever on the part of the Secretariat of the United Nations Industrial Development Organization (UNIDO) concerning the legal status of any country, territory, city or area or of its authorities, or concerning the delimitation of its frontiers or boundaries, or its economic system or degree of development. Designations such as “developed”, “industrialized” and “developing” are intended for statistical convenience and do not necessarily express a judgment about the stage reached by a particular country or area in the development process. Mention of firm names or commercial products does not constitute an endorsement by UNIDO.

FAIR USE POLICY

Any part of this publication may be quoted and referenced for educational and research purposes without additional permission from UNIDO. However, those who make use of quoting and referencing this publication are requested to follow the Fair Use Policy of giving due credit to UNIDO.

CONTACT

Please contact publications@unido.org for further information concerning UNIDO publications.

For more information about UNIDO, please visit us at www.unido.org

20066

Briquetting of Chromium
Ore Fines and Concentrates
for the Production
of High-Carbon Ferrochromium

FINAL REPORT

Prepared by
G.Surgutchev, Yu. Yusfin, N.Bakumova,
O.Ostrovskiy, V.Tikhomirov
for the
Government of Albania

CONTRACT No. 91/097
between
the United Nations Industrial Development Organization
and Internet Engineering

UNIDO PROJECT No. ST/ALB/89/801
Activity Code J13207

Final Report on Contract No.: 91/097

Project Title:

Briquetting of chromium ore fines and concentrates for the production of high-carbon ferrochromium

Project No.: SI/ALB/89/801

Synopsis:

The aim of this Contract is to prepare a preliminary process design including process flow-sheet, material balance, energy balance, raw material specifications, list of the main equipment with characteristics, for agglomeration plant of 100,000-300,000 t.p.y. of agglomerated chromium ores.

ABSTRACT

The requirements to charge materials used in high-carbon ferrochromium melting are presented.

The existing processes for the agglomeration of chromium-bearing ores and concentrates have been studied.

In order to select an optimal process for the agglomeration of the Albanian chromium raw material, a laboratory study has been carried out whose results are presented in the report.

The investigations performed have demonstrated an ability of making roasted pellets out of Albanian chromium concentrate without binders so that the finished product has the strength allowing its transportation and further processing.

A new (with reference to chromium-bearing materials) flow-sheet has been proposed for making Hybrid Pelletized Sinter (HPS-product) with a controlled degree of metal content. This product has favorable properties for making high-carbon ferrochromium.

The both products are possible to make on one and the same universal conveyor-type roasting machine with a specially prepared design (the know-how).

The report includes a preliminary design of the agglomeration process, a flow-sheet for making roasted pellets and metallized HPS-product, the structure of the plant, a list of main equipment with its basic parameters (the equipment is similar to this used at the existing agglomeration plants).

The data on material balance and energy expenditures for the process are given. The report is completed by conclusions and recommendations.

A conclusion is made that it is expedient to realize the agglomeration processes in the Albanian conditions. It requires to perform large-scale tests with a batch of Albanian chromium-bearing material in an amount of at least 1 tonne.

TABLE OF CONTENTS

1. INTRODUCTION
2. REQUIREMENTS TO CHARGE MATERIALS USED IN HIGH-CARBON FERROCHROMIUM MELTING
3. THE EXISTING PROCESSES FOR MAKING AGGLOMERATED RAW MATERIAL OUT OF CHROMIUM ORES IN DIFFERENT COUNTRIES (A SURVEY)
4. PRELIMINARY EXPERIMENTS WITH THE AIM OF SELECTION OF AN OPTIMAL PROCESS FOR THE AGGLOMERATION OF ALBANIAN CHROMIUM CONCENTRATES (ORE FINES)
 - 4.1. Characteristics of Source Materials
 - 4.2. Experimental Technique
 - 4.3. Experimental Results on Making Roasted Pellets out of Albanian Chromium Concentrate
 - 4.4. Results of Laboratory Experiments on Making Hybrid Pelletized Sinter (HPS-product) out of Chromite Concentrate
5. SPECIFICATION OF THE COMPOSITION AND PROPERTIES OF SOURCE MATERIALS AND THE PRODUCTS OF ALBANIAN CHROMIUM CONCENTRATE AGGLOMERATION
6. PRELIMINARY DESIGN OF THE PROCESS FOR MAKING PELLETS OUT OF ALBANIAN CHROMIUM CONCENTRATES
 - 6.1. A Flow-Sheet for Making Roasted Pellets and HPS-Product
 - 6.2. The Structure of the Agglomerating Plant, a List of Main Equipment and its Specification
 - 6.3. Material and Energy Balances for the Process of Albanian Chromium Concentrate Agglomeration. Main Technical-And-Economic Indices
7. CONCLUSIONS AND RECOMMENDATIONS

TABLE OF CONTENTS (Contd.)

TABLES

- 4.1. Chemical composition of chromium ores and concentrates
- 4.2. Experimental conditions for making roasted pellets out of Albanian chromite concentrate
- 4.3. 2^{4-3} design matrix for the problem of making roasted pellets out of Albanian chromite concentrate
- 4.4. Test variance calculation
- 4.5. Adequacy variance calculation
- 4.6. Results of mineragraphic examination

FIGURES

- 4.1. Nomographs showing the dependences between the strength of roasted pellets and various factors
- 4.2. Dependence of the strength of roasted pellets on the amount of silicate binder
- 4.3. Dependence of the strength of roasted pellets on the average size of pores
- 4.4. Dependence of the strength of roasted pellets on the average size of intervals between pores
- 4.5. Messbauer absorption spectra for initial concentrate, check experiment, and test 6

PHOTOS

- 4.1. Textures of the Albanian chromium ore
- 4.2. Microstructure of the Albanian chromium ore
- 4.3. Microstructure of roasted pellets
- 4.4. Macrophotos of ore-fuel pellets and HPS-product
- 4.5. Microphotos of ore-fuel pellets and HPS-product
- 4.6. Microphotos of HPS-product
- 6.1. Layout of the agglomeration plant

1. INTRODUCTION

There is a growing demand in all the world for high-quality stainless steel the production of which requires chromium raw materials. Quality chromium ore reserves decrease every year. The increase of the amount of fines in mining and a necessity for involving poor ores in the process with further enrichment result in the fact that the agglomeration problem becomes the most important. However, the problem of the agglomeration of chromium ores and concentrates is not solved thoroughly.

The specified problem has a number of aspects.

1) A necessity for high strength of agglomerated raw material which would allow its transportation. The method of agglomeration is determined in that case by the following factors:

- the composition (chemical, mineralogical, phase) of the source ore fines or concentrate;
- the feed size of primary powder (sometimes there is a necessity for its re-grinding);
- the maximal temperature of thermal treatment which in turn depends on the temperature of onset of Cr_2O_3 formation differing according to the type of ore, as well as on the amount of reducer in the charge required for high-carbon ferrochromium production.

2) Complexity of making agglomerated raw material out of chromium ores caused by their surface activity, in particular, by a high wetting ability of the surface.

Hydrate moisture continues to withdraw during the thermal treatment of chromium ores up to 1100-1200°C, thus preventing the process of sintering. Therefore, there is a necessity to determine for each type of ore a relation between the initial porosity of

agglomerated raw material ensuring moisture disposal with an optimal rate and the final porosity ensuring a sufficient strength of the finished product and satisfying the requirements of the consumer (in ferroalloy production).

This problem is also concerned with a selection of a grinding method (dry or wet) ensuring an optimal porosity of source agglomerated raw material.

3) A selection of binders and reinforces, and the utilization of enrichment tailings.

The study performed in MISA showed that the effectiveness of sintering depends on the charge composition (the content of Cr_2O_3 , Fe_2O_3 , FeO , CaO , MgO , Al_2O_3 , SiO_2 , and others). Using a special computer program designed in MISA, it is possible to find an optimal relation of the specified components for a given type of chromium ore (concentrate).

These relations could be changed by the introduction of different additions into the charge, including enrichment tailings, which favors the decrease of their accumulation in dumps.

By the use of fusible additions, it is possible to attain a decrease of the temperature of agglomerated raw material, which would make it possible to reduce the danger of the formation of high-toxic compounds containing Cr^{6+} .

It has been determined that the effectiveness of the influence of the specified additions reduces as the content of reducer in the charge rises. It calls for a necessity of solving the problem of determining the minimum content of reducer in the charge

which would not decrease the quality of raw material been obtained.

The Albanian Party requirements dictate that the raw material used in Albanian smelting furnaces should contain 38-40% Cr_2O_3 and have a granulometry of 80 mm.

The presence and further increase of Cr-bearing fines cause the quest for methods of its agglomeration.

Some laboratory tests for briquetting and pelletizing of concentrates have been carried out by the Institute of the Metallurgical Research of Albania.

We support the opinion of Mr. Martti Haani (the Expert Report on May 24-31, 1990, Vantaa, Finland) concerning the primary effort that should be put to pelletizing/sintering study rather than to briquetting one. However, a necessity of having 80mm lumps introduces additional difficulties into the problem of final selection of the agglomeration process, since it is impossible to make strong pellets with such a size.

An experimental batch of 10x10mm briquettes in an amount of 400 tonnes was manufactured in Albania in 1985. The charge contained 70% of fines and 30% of concentrate. Cement and coal resin were used as a binder. For attaining the required strength, briquettes were dried (endured) in open air for one month.

Besides, briquettes up to 50 mm in size were manufactured out of 1.5mm grain size concentrate by means of a cylindric hydraulic press with 10-tonne force. The following mixtures were used as a binder: 1) 1% lignin sulphonate; 2) 1.2% lignin sulphonate + 4.0% bentonite; 3) 2% molasses; 4) 1.0% molasses + 2% lime; 5) 5.0% bentonite. The strength of briquettes was good.

However, this process cannot be realized on industrial scale since industrial presses used for briquetting have much less forces, rather low productivity and high cost.

Studies on agglomerating chromium concentrates conducted by Metallurgic Institute in Elbasen gave a positive result. Therefore, according to Finnish experts' conviction, pelletizing should be the main process. After hardening roasting, pellets may be used both in Albania and for export to other countries, which will allows Albania to have much more profit comparing with the profit from concentrate export.

An opinion of Finnish experts that briquetting could not be even compared with pelletizing is fully identical to our conclusions.

During our first visit to Albania, the Albanian specialists and we came to a common opinion concerning the advantages of making pellets and HPS (hybrid pellets/sinter) product for the Albanian conditions. So a decision was taken to somewhat change the direction of working under the contract and to design a process of making pellets and HPS-product instead of briquetting process, and, moreover, bearing in mind the perspectives of the development of ferroalloy production in Albania, to increase the design output of future pelletizing plant up to 250,000 tonnes per year.

The proposed process for agglomerating chromium-bearing concentrates differs from similar processes in increased productivity and an ability of making two different products - pellets or sinters (HPS-product) - on one and the same machine.

Conveyor-type roasting machines are widely used in our country both in ferrous and non-ferrous metallurgy, so there is a

great experience of working on them as well as many experimental data.

The process of making pellets out of chromium-bearing concentrates was tested on semi-industrial scale. Wet pellets were made on a 3m diameter plate granulator; hardening roasting was carried out on a conveyor-type roasting machine with baking area of 10 m².

Making HPS-product out of iron ore concentrates was tested both on semi-industrial units (18 m²) and industrial machines (108 m² and 320 m²). The results of the tests are positive.

The purpose of the work, according to the terms of this contract, is a preliminary description of the process proposed for pelletizing of Albanian chromium fines (concentrate) based on the results of laboratory tests, the presentation of initial material and product specifications, a list of main equipment, and the results of preliminary calculations of material and energy balances for the process.

2. REQUIREMENTS TO CHARGE MATERIALS USED IN HIGH-CARBON FERROCHROMIUM MELTING

One of important technological processes in high-carbon ferrochromium melting is partial alloy refining from carbon via its interaction with chromium (and iron) oxides in slag and in ore. This interaction takes place as the charge moves deep into the furnace and drops of metal melt drain off (they form at $T > 1800$ K), and locates on the boundary between liquid metal and so called ore layer which looks as a 40-50mm wide viscous layer of charge and slag.

The formation of ore layer is caused by the use of lumpy chromium ore as one of the charge materials. It is evident that the amount of lumpy ore depends on the quality of ferrochromium being melted (upon the carbon content allowable in it).

Another important technological process in high-carbon ferrochromium melting is the formation of fluid slag ensuring the complete reduction of chromium and iron oxides. This slag must melt at a temperature of 50-70°C higher than the temperature of metal melting. Its optimal composition - 27-35% SiO_2 , 30-34% MgO , 26-30% Al_2O_3 , <6% Cr_2O_3 - is dictated by a constitution diagram for $\text{MgO-SiO}_2\text{-Al}_2\text{O}_3$ system. Such slag is produced via the use of quartzite as a part of the charge. The normal ratio of slag is 0.8-1.3, viscosity is 0.3-0.7 Pa/s, and melting temperature is 1833-1873 K.

It should be noted that the increase of silica content in the slag over 35% increases the viscosity of the slag, its ratio, electrode consumption, and the content of silicon in the slag.

The increase of MgO in the slag somewhat decreases the extraction degree of chromium. It is recommended to have MgO/Al₂O₃ ratio being not more than 1.6.

The analysis of high-carbon ferrochromium melting processes yields the following requirements to the charge materials:

- it is expedient to use lumpy chromium ore in the charge (10-70 mm or 20-80 mm) in an amount of at least 50% in FH650 ferrochromium melting and at least 20% in FHB00 ferrochromium melting;

- for optimal slag formation, it is expedient to use quartzite or other SiO₂-bearing materials. the total content of SiO₂ in the charge (in ore, flux, and ash) should be equal to 250-450 kg with respect to 1 g of alloy (depending on the content of Cr₂O₃ in the ore and the ratio of slag).

The technological requirements to ore specify the Cr₂O₃/FeO ratio (>3-3.5), the content of sulphur (<0.05-0.08), phosphorus (<0.05), and moisture (<4%). Bean and semi-coke should have an ash content of <11-13%, the content of total sulphur of <0.5%, the yield of volatile matter of <10-12%, that of fines (less than 10 mm) of <5-15%, and that of lumps (more than 25 mm) of <10%.

3. THE EXISTING PROCESSES FOR MAKING AGGLOMERATED RAW MATERIAL OUT OF CHROME-BEARING ORES IN DIFFERENT COUNTRIES (A SURVEY)

The world practice, the analysis of literature, as well as that of patent information and catalogues of companies producing Cr-bearing raw material has been demonstrated that a process for making pellets out of chromite ores in shaft furnaces ("Outokumpu", Finland) is the most wide-spread. The process of "Outokumpu" is used at plants of Greece, Philippines, India, Turkey, and other countries.

At the plant in Tornio (Finland), ferrochromium is melted of hot charge pre-heated in a rotating furnace at 1000-1100°C. Cr-bearing pellets of 10-20 mm in size are made from wet grinded chromite ore (concentrate, 85% of -0.074mm fraction) containing about 40% Cr₂O₃ and 7% SiO₂ with the addition of 1% binder (bentonite clay). The pellets are roasted in shaft furnaces (having an annual production rate of 140,000 tonnes) at 1200-1400°C. The strength of roasted pellets is 200-300 kg/pellet.

Processes used for making Cr-bearing pellets at plants of Sweden, Germany, Japan, and other countries differ from the above considered in a method for ore (concentrate) grinding, the final granulometric composition of grinded material, initial humidity of concentrate and pellets, types of additions used in the charge (binders etc.), modes of pelletizing and drying, as well as in the modes of raw pellets roasting and finished product cooling.

For example, at "Ferrolegeringar" plant (Irolhettan, Sweden) ore (concentrate) is grinded in rod and ball mills below to a grain size of -0.2 mm (one third of total amount has a grain size

of -0,07 mm). At "Gesellschaft für Electrometallurgic, GFE" plant (Waiswailer, Germany) ore has a humidity of at most 10% before grinding and a grain size of -1 mm after grinding. At "Nippon kindzoku to kagaku" plant (Japan) a pre-dried mixture of chromite ore and reducer is grinded in a ball mill below to a grain size of -0.15 mm.

Besides bentonite ("Outokumpu"), additions to the charge of pellets may include slaked lime, silicon material from filters behind furnaces for melting ferrochromium silicon ("Ferrolegeringar"), coke breeze and gas cleaning dust ("Ferrochrome Philippines"). At "Gesellschaft für Electrometallurgic, GFE" plant there is a practice of making wet pellets without binders. The strength of wet pellets with 1% bentonite or 2% slaked lime addition is higher and equal to 1.1-1.5 kG/pellet.

The size of pellets produced at plants of different companies varies in the range of 5-50 mm, but normally is not greater than 15-20 mm.

Modes for hardening of pellets made at different plants vary greatly. For instance, in Sweden the priority belongs to a roasting-free (autoclave) mode for hardening of pellets made of chromite fines by means of a Kabo process. The annual capacity of such a unit is 150,000 tonnes. At "Gesellschaft für Electrometallurgic, GFE" plant pellets are hardened on a LEPOL unit (grate/rotating furnace) with an output of 250 tonnes/day. 6-50mm diameter pellets roasted at 1300-1450°C has a strength of 70-250 kG/pellet. 10-25mm diameter pellets roasted at 1500-1600°C has a mean strength of 250 kG/pellet. Moreover, it has been established that a mode of cooling has a great impact on the strength of

roasted chromium pellets, and only slow cooling for several hours keeps an initial strength. After air cooling the strength of pellets decreases by 50%; after compressed air cooling and water cooling the strength of pellets decreases respectively by 40% and 30% (when leaving the furnace). At "Nippon Kōtan" plant (Toyama, Japan) pellets are roasted in a ring vertical furnace produced by Associated Portland Cement Manufacture (Great Britain) and having an annual capacity of 140,000 tonnes. The temperature of roasting is 1110-1150°C. At plants of "Syova denko", "Nippon kindzoku to kagaku" (Toyama), and "Nippon dzyu kataku" (Hyusyu, Japan) pellets are roasted with the addition of fuel into the charge at 1300-1450°C, in particular, after pre-heating of pellets in a shaft furnace ("Syova denko"). In this process about 60% of chrome and up to 90% of iron contained in oxides is reduced.

The data on making Cr-bearing raw material on conveyor-type roasting machines are absent. However, the study conducted by MISA on making pellets in pilot-production conditions out of chromite concentrates of Donskoy mining works has demonstrated an ability of using conveyor-type roasting machines for making pellets. A process has been proposed and is designed now for making Cr-bearing sinters (pellets/sinter hybrid product), i.e. so called HPS-product. This process has been tested on industrial conveyor-type roasting machines in making sinters out of iron ore raw material.

Making pellets with rather high strength at rather low temperatures has become possible due to the control of the surface properties of chromite concentrates before pelletizing, the optimization of the composition of pellets charge (by means of regulating the relationships between the content of different compo-

nents in the charge via the introduction of fusible additions), and as a result of finding an optimal relation between the composition of the charge of pellets (sinters) and the modes of their thermal treatment.

In order to determine an ability of applying this process for making agglomerated raw material out of Albanian ores (concentrates), a series of laboratory tests and the processing of their results have been conducted according to a technique developed at the Department of Ore Thermal Processes of MISA.

4. PRELIMINARY EXPERIMENTS WITH THE AIM OF SELECTION OF AN OPTIMAL PROCESS FOR THE AGGLOMERATION OF ALBANIAN CHROMIUM CONCENTRATES (ORE FINES)

4.1. Characteristics of Source Materials

Chemical Composition

Chemical analysis of Cr-bearing ores and concentrates of Albania has been carried out, as well as that of additions used in the charge of pellets.

The data on the chemical composition of Cr-bearing materials of Albania presented by the Albanian Party are given in Table 4.1.

In order to determine the type of Cr-bearing mineral and gangue, polished and transparent sections have been made for mineralographic and crystallooptic analysis.

*Petrographic Analysis of Albanian Chromium Ore**

Ore Texture. The examination of the texture was conducted by reflected light with small magnifications. The three types of texture have been detected: massive, impregnated, and streaky.

In massive texture (Photo 4.1), chromite grains contact with each other, and crystals of silicate minerals of barren rock are to be found only on separate sections between the grains. This

* The petrographic analysis has been performed by E.F.Vegman, Professor at the Department of Ore Thermal Processes of MISA, Doctor of Technical Sciences.

Table 4.1

Chemical composition of chromium ores and concentrates

Ore Deposit	SiO ₂	Al ₂ O ₃	MgO	Cr ₂ O ₃	Fe ₂ O ₃	FeO	Others	Cr/Fe	
Mono-mineral	Kraste	0.80	36.05	17.12	32.06	2.11	11.29	0.57	2.14
	Studenti	1.10	21.70	15.45	44.66	3.83	12.95	0.67	2.39
	M.Botoce	0.95	20.33	11.93	47.53	1.33	17.49	0.44	2.24
	J.Politekniki	0.50	10.21	14.24	60.52	2.41	12.06	0.06	3.74
	Bulqize	0.50	12.36	15.71	57.20	2.35	11.56	0.32	3.68
	M.Trigjeprave	0.30	8.46	11.22	61.36	1.93	16.53	0.2	3.26
Bulqize	10.94	7.34	23.07	40.81	10.65	7.19	3.4		
Bulqize	9.78	7.01	23.23	40.54	11.76	7.68	3.09		
Bulkize**	8.43	8.80	20.16	47.13	10.62	2.74	2.12	3.37	
Bater	10.55	8.07	23.53	40.48	10.35	6.42	3.29		
Bater	7.82	7.15	23.35	42.17	11.4	5.56	1.71		
Bater**	3.13	3.47	19.15	47.5	11.25	1.30	2.6	1.25	
	13.0	15.7	23.0	25.0	2.5	9.3	10.4	1.62	
	4.0	21.0	17.5	37.0	15.5	-	3.7	2.19	

3* Chromium concentrate

texture belongs to rich chromium ore which is the most valuable. Its presence is an indication of the late magmatic genesis of the ore body from the Albanian deposit. Silicate minerals have been the first to be crystallized here from the magma, which corresponds to the conditions of cooling ultrabasic silicate magma saturated with gases. The residual oxide melt has been pressed back by the front of growing silicate crystals into spaces, voids, and cracks among the silicate masses already solidified. At the final (late magmatic) phase chromite has been crystallized in a form of massive monolithic sections.

Impregnated and streaky textures are here the intermediate ones among the blocks of massive chromium ores and blocks formed almost solely by silicates. Chromite grains are uniformly impregnated in the mass of silicates which form here and there strips up to 4-5 mm wide appeared as a result of the gravitational differentiation of the magma, i.e., during lowering of more heavy chromite crystals in relatively more light silicate liquid magma.

Ore Structure. Irrespective of texture, the structure of the ore may be described as cataclastic structure of crushing. Under the influence of great mountain pressure (dynamomorphism), chromite grains have been cracked with the formation of acute-angled debris and splinters (Photo 4.2). Grains of olivine, playing in this ore the role of barren road, undergo similar changes. The second component of barren road, serpentine (chrysotyl), has not been affected by cracks. The point is that extremely hard chromite and olivine (the hardness is 7.5 and 7 their numbers respectively) are at the same time fragile, whereas soft serpentine (the hardness is 3) has some plasticity. It is interesting that debris of

large chromite and olivine grains do not change their position in the space while failing and save parallelism within the bounds of the former grain contour. It is extremely clearly seen with respect to olivine grains - all the splinters of one former large grain become simultaneously dim during the rotation of microscopic stage.

Mineralogical Composition. The study of mineralogical composition was conducted by the methods of mineragraphy and crystallooptics. According to these data, chromite is here the only ore mineral.

Chromite/chromespinelide, $(\text{Fe},\text{Mg})(\text{Al},\text{Cr})_2\text{O}_4$ is detected in polished sections by reflected straight light in a form of isometric grains, rounded and oval nodules. It is badly buffed due to the pitful structure of the surface. The reflecting power is 14 %. It is isotropic (cubic syngony). Double-reflection is absolutely absent. It is gray in reflected light. In transmitted light, it is translucent as dark-red in very thin sections. In polished sections, the internal reflexes are brown-red. It is non-magnetic; is not drawn by a steel needle; is not etched by nitric and hydrochloric acids as well as by $\text{K}(\text{OH})$.

Barren Rock. In reflected and transmitted light, it is clearly seen that in all cases it consists of two phases - jointing mass of olivine grains and serpentine fibres positioning between the grains and along cracks inside them. The process of serpentinization of olivine is rather typical for ultrabasic rocks on the whole. In that case the product of olivine failure is a silicate from the group of micas - serpentine (ophite), more exactly,

its fibrous version - chrysotyl. The data of more fine diagnostics of barren rock are as follows.

1) Olivine: $(\text{Mg,Fe})_2\text{SiO}_4$. Forms colorless isometric, rounded grains broken up by irregular cracks. Sometimes there are wide-table crystals. There is high relief, sharply pronounced shagreen surface being noticeable even without diaphragming. Weak vague sealness is found only on a few of large olivine grains. It is optically anisotropic; there is straight extinction with respect to sealness. There is high double-refraction: $N_o - N_p = 0.036 \dots 0.038$ (measured with the help of quartz wedge by the method of compensation).

2) Serpentine (ophite): $\text{Mg}_3[\text{Si}_4\text{O}_{10}](\text{OH})_6$. It is represented here by its fibrous version - chrysotyl. It is colorless; there is straight extinction with respect to the axes of filaments on rectilinear sections. There is double-refraction: $N_o - N_p = 0.011 \dots 0.013$ (measured by quartz wedge). It is optically positive.

4.2. Experimental Technique

Preparation of Source Materials and Making Wet Pellets out of Chromite Concentrate

The most suitable charge composition and roasting conditions for making pellets out of Albanian chromite concentrate have been determined by the method of mathematical experiment design. The compressive strength of roasted pellets has been selected as the main parameter of optimization.

The content of additions A, B, C, D (the know-how), the time of heating and the time of isothermal holding of pellets at high temperature were selected as variation factors.

During the investigations on making Cr-bearing pellets, all the source materials (the charge components) were subjected to primary crushing with further re-grinding in a mechanical agate mortar down to -0.15 mm fraction.

Then 8 different charges differing in the type and quantity of additions (Table 4.2) were composed and thoroughly intermixed. Wet pellets were obtained of humidified charge in equal conditions by 2-minute rolling.

High-Temperature Roasting of Cr-Bearing Pellets

After a preliminary drying at 120°C for 2 hours, Cr-bearing pellets were subjected to high-temperature hardening roasting. The roasting was conducted in a tube silite furnace constructed by MISA in air atmosphere at 1300°C. Pellets were charged in a Ni-Cr basket and lowered in the furnace heated up to the required temperature by means of a special mechanism allowing to vary the rate. The duration of heating (lowering) and holding at high temperature varied and was equal to 8 and 20 minutes (Table 4.2). The duration of cooling (hoisting) was equal to 15 minutes in all tests.

The temperature in the furnace was monitored by a Pt-Rh-30/6 thermocouple. A KSP-4 potentiometer was used as a secondary instrument.

The compressive strength of pellets was determined on a mechanical press.

In order to investigate the microstructure of pellets, polished sections were manufactured of them.

Instrumental Methods

The microstructure of roasted pellets was investigated by reflected light on microscopes Neophot-21, Amplival-pol-4, and MIN-9 with a magnification of 50-1350 powers.

Source Cr-bearing materials and roasted pellets were analyzed by a NTA-1024 analyzer based on the method of nuclear gamma-resonance spectroscopy. The source was ^{57}Co in Cr matrix.

The interpretation of spectra was carried out by a specially designed program on an IBM-compatible computer.

The control of phase composition was conducted also by a DRON-1 X-ray diffractometer.

Changes made during the process of concentrate heating were studied on a Q-derivatograph (thermal analyzer) in the thermal range 20°C-1050°C in air atmosphere at the rate of specimen heating of 10 degrees per minute.

4.3. Experimental Results on Making Roasted Pellets out of Albanian Chromium Concentrate

Dependence of the Strength and Structure Parameters of Roasted Cr-Bearing Pellets on Different Factors

The investigations have been conducted with the use of the method of mathematical experiment design. A technique for making

wet and roasted pellets was presented earlier. Experimental conditions are given in Table 4.2.

Table 4.2

Experimental conditions for making roasted pellets out of Albanian chromite concentrate

Factors	A ad- dition, %	B ad- dition, %	Heating time, min.	C ad- dition, %	D ad- dition, %	Isothermic holding time, min.
Code	X_1	X_2	X_3	X_4	X_5	X_6
Basic level (0)	3	5	14	1	0.25	14
Variation intervals (I)	1	5	6	1	0.25	6
Upper level (+1)	4	10	20	2	0.50	20
Lower level (-1)	2	0	8	0	0	8

Tables similar to Table 4.2 are standard when used at the stage of problem statement. The factors are coded here by the carry of the origin of coordinates into the center (basic level) and the selection of a scale in factor variation units. Coded factor values (x_i) are related to natural ones (X_i) as follows:

$$x_i = \frac{X_i - X_{i0}}{I}$$

where X_{10} is the natural value of the factor at the basic level; I is the natural value of variation interval.

The temperature of roasting was 1300°C, the duration of pellets cooling was 15 minutes.

Once optimization parameters and variation factors had been selected and basic levels had been established for them, it was possible to adopt a possibility to estimate linear effects by means of a fractional replicate selected. 2^{6-3} fractional replicate selected was represented as a design matrix (Table 4.3). Factor values +1 and -1 are replaced here by symbols "+" and "-".

Table 4.3

2^{6-3} design matrix for the problem of making roasted pellets out of Albanian chromite concentrate

Test ; number ;	Factors							y
	x ₀	x ₁	x ₂	x ₃	x ₄	x ₅	x ₆	
1	+	+	+	+	+	+	+	140
2	+	+	-	+	+	-	-	33
3	+	-	+	+	-	+	-	148
4	+	-	-	+	-	-	+	92
5	+	+	+	-	-	-	-	61
6	+	+	-	-	-	+	+	208
7	+	-	+	-	+	-	+	125
8	+	-	-	-	+	+	-	164

Notation used in Table 4.3 is as follows. $X_1 - X_6$ are factors which affect the properties of pellets (variation factors in Table 4.2); y is the compression strength of pellets (optimization parameter), kg/pellet.

As an example, the calculation of regression coefficients and the statistical analysis of an equation describing the dependence of the strength of roasted pellets on the factors selected is presented. The results given in Table 4.3 (compressive strength of pellets, y , kg per pellet) have been obtained as a result of tests in accordance with the design matrix.

The regression coefficients of a linear equation describing the response surface in a local section situated near the basic level were calculated by the following formula:

$$b_1 = \frac{\sum_{u=1}^N x_{1u} y_u}{N},$$

where x_{1u} is the value of x_1 in the u -th test; y_u is the value of the optimization parameter (the compressive strength of pellets in this case) in the same test.

A regression equation describing a dependence of the strength of roasted pellets on the variation factors is as follows:

$$y = 121 - 11x_1 - 3x_2 - 18x_3 - 6x_4 + 44x_5 + 20x_6$$

A variance characterizing an error in determining the coefficients of regression ($S^2_{b_i}$) is found from the expression

$$S^2_{b_i} = \frac{S^2_y}{N},$$

where $S^2_{\bar{y}}$ is the variance of the test; N - the number of tests.

The results of test variance calculation are given in Table 4.4.

Table 4.4

Test variance calculation

Test number (u)	Repetition number (j)	Strength (y_{uj})	Average strength in the u-th test	$\Delta y_{uj} = y_{uj} - \bar{y}_u $	Δy^2_{uj}	$\sum_{j=1}^n \Delta y^2_{uj}$																																																																																	
1	1	139	140	1	1	5																																																																																	
	2	142		2	4		2	1	30	33	3	9	18	2	36	3	9	3	1	151	148	3	9	13	2	146	2	4	4	1	94	92	2	4	5	2	91	1	1	5	1	63	61	2	4	13	2	58	3	9	6	1	210	208	2	4	5	2	207	1	1	7	1	128	125	3	9	18	2	122	3	9	8	1	160	164	4	16	25	2	167	3	9	$S^2_{\bar{y}}$			
2	1	30	33	3	9	18																																																																																	
	2	36		3	9		3	1	151	148	3	9	13	2	146	2	4	4	1	94	92	2	4	5	2	91	1	1	5	1	63	61	2	4	13	2	58	3	9	6	1	210	208	2	4	5	2	207	1	1	7	1	128	125	3	9	18	2	122	3	9	8	1	160	164	4	16	25	2	167	3	9	$S^2_{\bar{y}}$						102								
3	1	151	148	3	9	13																																																																																	
	2	146		2	4		4	1	94	92	2	4	5	2	91	1	1	5	1	63	61	2	4	13	2	58	3	9	6	1	210	208	2	4	5	2	207	1	1	7	1	128	125	3	9	18	2	122	3	9	8	1	160	164	4	16	25	2	167	3	9	$S^2_{\bar{y}}$						102																			
4	1	94	92	2	4	5																																																																																	
	2	91		1	1		5	1	63	61	2	4	13	2	58	3	9	6	1	210	208	2	4	5	2	207	1	1	7	1	128	125	3	9	18	2	122	3	9	8	1	160	164	4	16	25	2	167	3	9	$S^2_{\bar{y}}$						102																														
5	1	63	61	2	4	13																																																																																	
	2	58		3	9		6	1	210	208	2	4	5	2	207	1	1	7	1	128	125	3	9	18	2	122	3	9	8	1	160	164	4	16	25	2	167	3	9	$S^2_{\bar{y}}$						102																																									
6	1	210	208	2	4	5																																																																																	
	2	207		1	1		7	1	128	125	3	9	18	2	122	3	9	8	1	160	164	4	16	25	2	167	3	9	$S^2_{\bar{y}}$						102																																																				
7	1	128	125	3	9	18																																																																																	
	2	122		3	9		8	1	160	164	4	16	25	2	167	3	9	$S^2_{\bar{y}}$						102																																																															
8	1	160	164	4	16	25																																																																																	
	2	167		3	9		$S^2_{\bar{y}}$						102																																																																										
$S^2_{\bar{y}}$						102																																																																																	

A confidence interval for the coefficients of regression are calculated by the formula:

$$\Delta b_1 = \pm t_{\alpha, N} \cdot S_{b_1},$$

where t is a Student t -test; α is a significance level (the probability of practically impossible events) assumed to be equal to 0.1.

Thus,

$$\Delta b_1 = \pm 1.86 \sqrt{\frac{102}{8}} = 6.6.$$

Therefore, for absolute values of the coefficients of regression exceeding 6.6, all linear effects should be recognized to be statistically significant.

After the coefficients of regression had been calculated and its significance had been tested, a statistical analysis of the regression equation was carried out. For this purpose, a hypothesis was tested on adequacy of this equation, i.e., a problem was considered whether the linear equation obtained may be used or there is a necessity of a more complicated model.

For testing for goodness of fit, the variance of adequacy was calculated:

$$S^2_{\text{ad}} = \frac{\sum_{i=1}^N (y_{i \text{ calc}} - y_{i \text{ exp}})^2}{N-k-1},$$

where $y_{u \text{ calc}}$ is the value of the optimization parameter in the u -th test predicted by the regression equation; $y_{u \text{ exp}}$ - the value of the parameter in the same test determined from the experiment; k - the number of variation factors.

The results of adequacy variance calculation are given in Table 4.5.

Table 4.5

Adequacy variance calculation

Test number:	y_{exp}	y_{calc}	$\Delta y = y_{\text{calc}} - y_{\text{exp}} $	Δy^2
1	140	153	13	169
2	33	25	8	64
3	148	141	7	49
4	92	99	7	49
5	61	67	6	36
6	208	201	7	49
7	125	117	8	64
8	164	171	7	49
				529

The adequacy variance was equal to:

$$S^2_{\text{ад}} = \frac{529}{8-6-1} = 529.$$

A hypothesis on adequacy was tested using Fisher's F-ratio test:

$$F_{calc} = \frac{S^2_{ad}}{f_2 : f_1 \quad S^2_y}$$

where f_2 and f_1 are the numbers of degrees of freedom in finding the variances of adequacy (S^2_{ad}) and the test (S^2_y).

A hypothesis on adequacy of linear model may be accepted if the calculated value of F-ratio test (F_{calc}) is not greater than the table one (F_{tab1}) for the significance level selected.

In our case,

$$F_{calc} = \frac{529}{1;8 \quad 102} = 5.19.$$

Having 5-percent significance level ($\alpha = 0.05$), the table value of F-ratio test is

$$F_{tab1} = 5.35;$$

for $\alpha = 0.01$,

$$F_{tab1} = 11.41.$$

Since $F_{calc} < F_{tab1}$, a hypothesis on adequacy of linear model is not rejected, and it may be used at further design stages and, in particular, for finding a direction of movement along the gradient to an optimum.

In this stage of experiments, the regression equation obtained (intermediate one) was applied for constructing nomographs given in Fig. 4.1, a-f.

Table 4.6

Results of mineragraphic examination

Test number	Characteristic of macrostructure	Fraction of sintered area, %	Porosity, % (vol.)			Average pore size, μm	Average size of intervals between pores, μm	Amount of silicate binder, %	Strength of pellets, kg/pellet
			of sintered part	of unsintered part	total				
1	homogeneous	100	60.3	-	60.3	89	111	4.8	140
2	heterogeneous	20.0	72.7	96.7	91.9	64	171	1.3	33
3	homogeneous	100	60.9	-	60.9	60	138	3.0	148
4	heterogeneous	15.0	57.9	86.8	83.6	81	150	1.7	92
5	heterogeneous	23.0	70.0	94.2	84.7	74	164	0.4	61
6	homogeneous	100	59.8	-	59.8	82	104	5.8	208
7	homogeneous	100	58.6	-	58.6	96	118	3.6	128
8	homogeneous	100	54.9	-	54.9	80	126	3.7	164

The numeration of samples corresponds to the conditions of the tests presented in Tables 4.2-4.3

Mineragraphic Examination of Roasted Pellets

In order to find a relation between the microstructure of pellets and their strength, thirty polished sections were studied. The study included the determination of the amount of silicate binder.

The results of the study are given in Table 4.6.

As the examination showed, the microstructure of pellets in test 2 is a number of little parts of source concentrate which are situated rather separately.

Pellets in tests 1, 3, 6, 7, and 8 are sintered in the whole volume and have rather dense structure with a marked amount of silicate binder (3-6%), which allows us to arrive at a conclusion concerning the liquid-phase nature of sintering (Photo 4.3, a).

The study of polished sections for tests 6 and 8 showed that ore grains are carburized with each other by silicate binder locally. In the rest of the volume sintering had been proceeded mainly in solid phase (Photo 4.3, b).

The melt obtained due to additions and forming silicate binder while being cooled is, obviously, heterogeneous in its composition, which is indicated by the thickness of binder exuded.

The examination of polished sections for roasted pellets made it possible to determine a strict relation between the strength of pellets and the amount of silicate binder in them, the average size of pores and intervals between them (Fig. 4.2-4.4).

Results of Derivatographic Examination

The study of Cr-bearing concentrate behavior during its

heating in oxidizing atmosphere was performed on a Q-derivatograph made in Hungary. The conditions of examination were as follows: the initial temperature was 20°C, final temperature was 1050°C, weight of the sample was 0.5597 g, crucible was platinum, rate of heating was equal to 10 degrees per minute. The sensitivity was equal to 1/5 for DTA, 1/10 for DTG, and 200 mg for TG.

The analysis of the derivatogram showed that moisture adsorbed from air (0.002 g) was being disposed up to 80°C. During further heating up to 810°C, a slow disposal of hydrate moisture appeared to take place. A total loss of moisture in that range was equal to 0.014 g.

Oxidation of the sample practically was not to be observed.

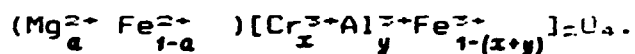
The results obtained corroborate a conclusion that the hardening of pellets made of Cr-bearing ores and concentrates proceeds inefficiently due to the absence of oxidizing processes, so an increase in the strength of roasted pellets requires either the elevation of the temperature of roasting or the introduction of fusible additions simulating the formation of the melt.

A derivatographic examination (oxidizing atmosphere, different heating rates) of specimens up to 1300°C is also performed. A certain increase in the weight of specimen was noticed from 1050 to 1200°C, which is caused by the processes of rearrangement and ordering in spinel lattice. This phenomenon agrees with the results of Messbower analysis.

*Results of the Examination of Chromium Concentrates and Roasted Pellets Performed by the Method of Nuclear Gamma-Resonance Spectroscopy**

The examination of Albanian chromium concentrates performed by the method of nuclear gamma-resonance spectroscopy corroborated the fact that the type of the lattice formed by the main component, chromium oxide, is determined rather by the content of iron, magnesium, etc., than by the total content of chromium. The main minerals, which, as was established, constitute Albanian chromium ores and concentrates, are chromite and compounds related to the continuous isomorphous chromite-spinel series of solid solutions.

Chromite contained in Albanian ores does not in fact differ in its crystallochemical structure from chromites contained in Kazakh ores (Donskoe deposit) and has the following crystallochemical formula:



The total amount of solid solutions in the series $(\text{Mg,Fe})\text{Al}_2\text{O}_4 - (\text{Mg,Fe})\text{Cr}_2\text{O}_4$ is about 70 %, the total amount of solid solutions of the type $(\text{Mg,Fe})\text{Fe}_2\text{O}_4$ is about 3-10 % (the content of Fe^{2+} in solid solutions does not depend on the content of Fe^{3+}).

However, in contrast to Kazakh ores, as the study by the method of X-ray diffractometry shown, Albanian chromium concentrates contain, besides chromites, a small amount of α -solid

* The examination has been performed with the aid of Yu.B.Voitkovsky, Professor of Moscow Mining Institute, Doctor of Technical Sciences

solutions in Cr_2O_3 of iron (Fe^{2+}), aluminium (Al^{3+}) as well as the hydroxides and carbonates of iron, magnesium, and various aluminosilicates contained in barren rock.

The method of Mossbauer spectroscopy has been applied for examining both the specimens of the source Albanian ore (concentrate) and of roasted pellets of the check series and also of these corresponding the conditions of test 6 (see Table 4.3). The spectra are presented in Fig. 4.5, a-c.

As the preliminary analysis of Mossbauer spectra of absorption for the examined specimens has shown, chromite itself does not undergo phase changes after high-temperature oxidizing roasting. However, the degree of spinel lattice turning, its parameter, and the presence of defects change. Moreover, α -solid solution contained in the source concentrate comes into interaction with iron and magnesium oxides appearing as a result of decomposition under heating of the hydrates and carbonates of the relevant metals. The products of the specified interaction are assimilated by the lattice of chromite, which also corroborates the analysis of spectra presented.

In Fig. 4.5, a-c, horizontal lines represent the amplitudes of the corresponding Lorentz lines marked for visual convenience as halves of their real values. Under the spectrum, the error of this decomposition is marked in units of standard deviation for every channel.

According to the conclusions of the work*, we have interpreted the specified decomposition as follows: doublet D corre-

* M. Robbins, G.K. Wertheim, R.C. Sherwood, D.H.E. Buchanan. Magnetic Properties and Position Distribution in the System FeCr_2O_4 - Fe_2O_3 ($\text{Fe}^{2+}\text{Cr}_{2-x}\text{Fe}^{3+}_x\text{O}_4$). - Phys. Chem. Solids, 1971, v.32, p.717-729.

sponds to Fe^{2+} ions being at octapositions of chromespinelide; doublet II corresponds to Fe^{2+} ions at tetrapositions of chromespinelide; singlet (s) corresponds to Fe^{2+} ions appearing as interstitial atoms in octahedron positions of the spinel structure.

A similar picture of decomposition (two doublets and one singlet) takes place in all the spectra of the specimens been the subject of a certain thermal treating and with various additions, which demonstrates a uniformity of the proceeding processes and, on the other hand, corroborates the correctness of the model accepted and the policy of decoding. However, the isomeric shift and quadrupole separation of subspectra in the decomposed spectra differ considerably for the specimens after their high-temperature treating, as compared with a specimen of source concentrate, which indicates a considerable distortion of chromespinelide lattice resulting from intensive diffusion processes accompanying phase changes initiated by high temperature as well as from introducing pellets of fusible additions into the charge. This, probably, may explain a considerable growth of pellets strength in certain conditions.

4.4. Results of Laboratory Experiments on Making Hybrid Pelletized Sinter (HPS-product) out of Chromite Concentrate

As a result of the laboratory investigations conducted, an ability has been shown to make roasted pellets of sufficient strength out of Albanian chromium concentrate which would be suitable both for transportation (in the case of export) and utiliza-

tion as an addition to the charge of ferroalloy furnaces (in combination with lumpy ore).

However, for making high-carbon ferrochromium, a lump of about 80 mm in size is required. For making such type of raw material, the following process is suggested.

Cr-bearing green pellets (10-12 mm in size) were produced from the chromium ore (Donskoe deposit) which have a similar composition (mainly content of Cr_2O_3) to the Albanian ores.

The charge of green pellets consisted of Cr-ore fines, solid fuel (coke), and different fusible additions and did not include binders (such as bentonite etc.). There were 6 kinds of charges.

Green balls were charged into a tubular furnace, where they passed through drying, indurating (1250-1300°C), and cooling zones.

The kind of finished product (microstructure, phase composition, porosity, density, etc.) depended on the charge kind, specifically on the kind of fusible additions.

The finished product was represented by pellets having a granulometry of 10-12 mm or "sinter" (HPS-product) having different granulometry, porosity, and density (Photo 4.4).

Then products were put into melted (at 1600°C) slag with composition of high-carbon ferrochromium production. It was found that the dissolving rate of HPS-product is comparable to chromium ore lumps.

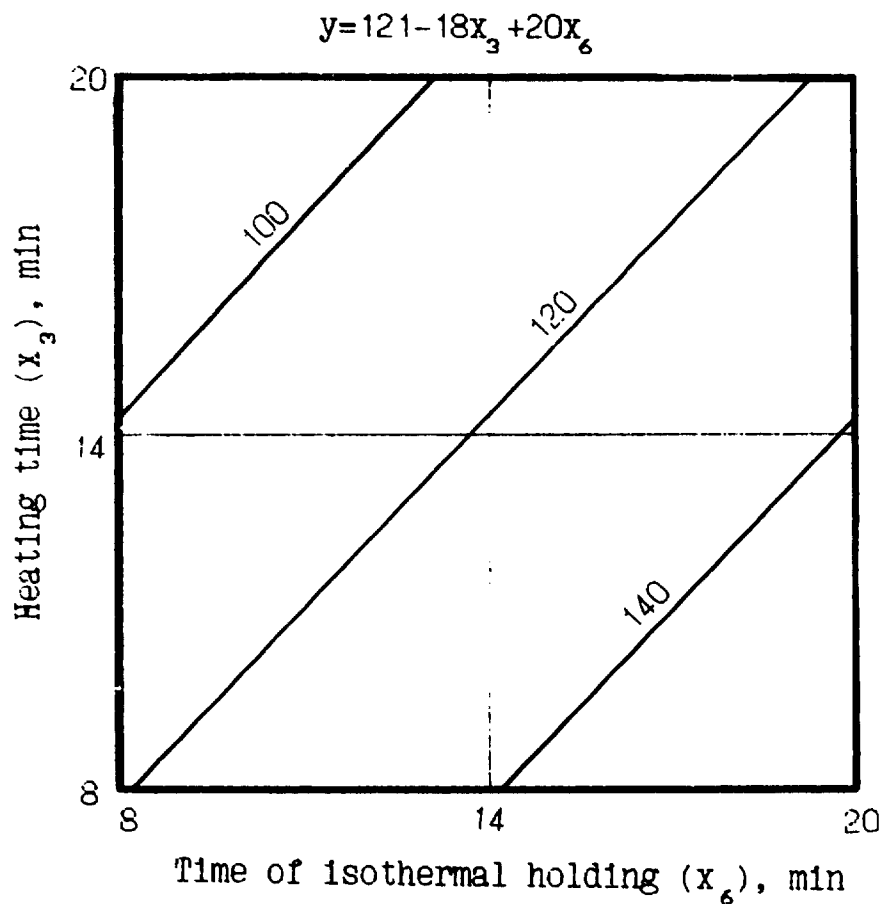
It was clarified that the properties of the HPS-products from the viewpoint of Fe-Cr smelting process were superior to those of pelletizing.

The analysis of microstructures ($\times 500$) of ore-fuel pellets and HPS-products have shown that the amount of metallic phase in the HPS-product is more than that of pellets (Photo 4.5-4.6).

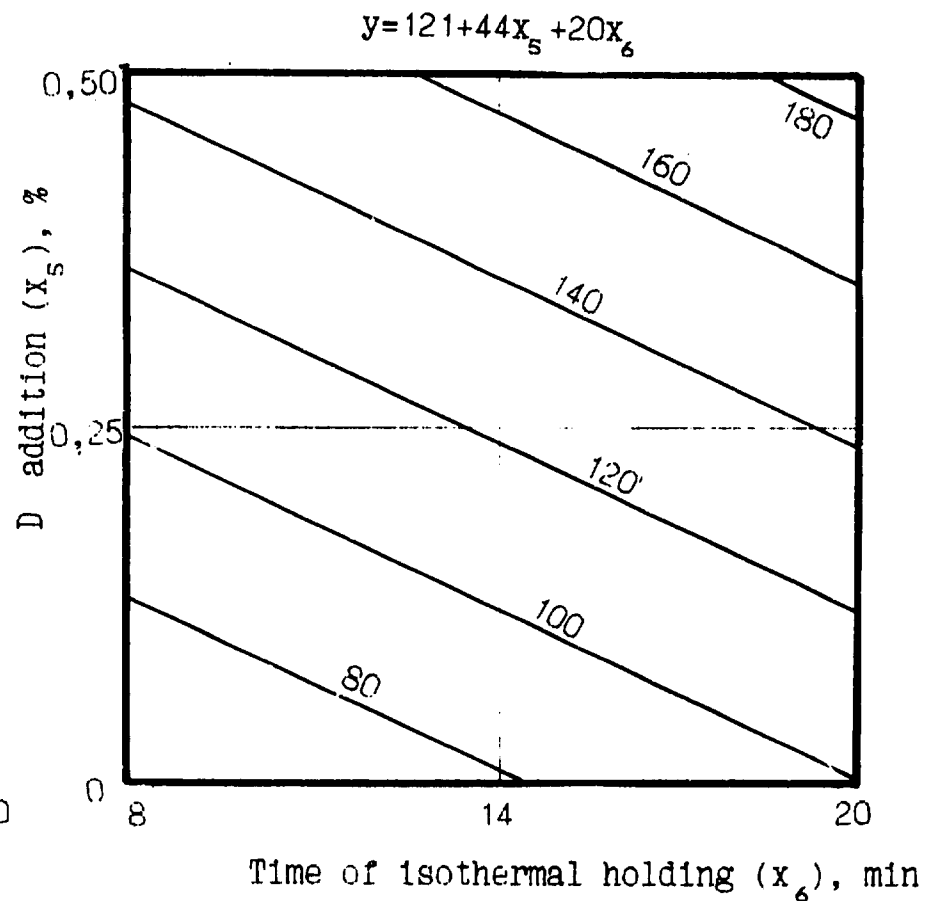
In the HPS-process, as the mineral phase formation depends on combustion heat resulting from the added solid fuel as well as the conventional sintering process, the combustion efficiency during "sintering" is quite important. When green balls which are charged in a travelling grate change to products by passing through drying, indurating, and cooling zones, both material and heat transfer phenomena occur simultaneously in the bed. Consequently, the study of these processes is quite necessary.

Various rate parameters, physico-chemical constants, and thermal functions determined during laboratory experiments will be used in the mathematical models, which will be the main guide to operate the process on the commercial plant conditions.

Fig. 4.1. Nomographs showing the dependence between the strength of roasted pellets and various factors



a

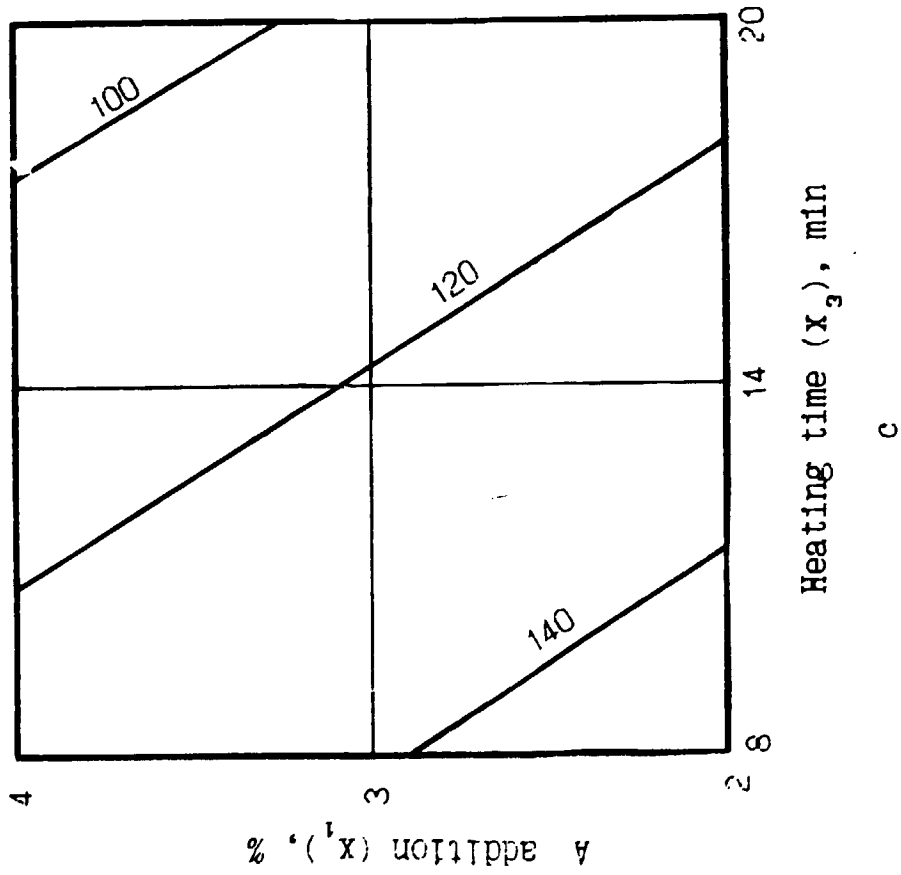


b

Numbers on the graph are the values of roasted pellets strength, kg/pellet

Fig. 4.1 Cont

$$y = 121 - 11x_1 - 18x_3$$



$$y = 121 - 11x_1 + 44x_5$$

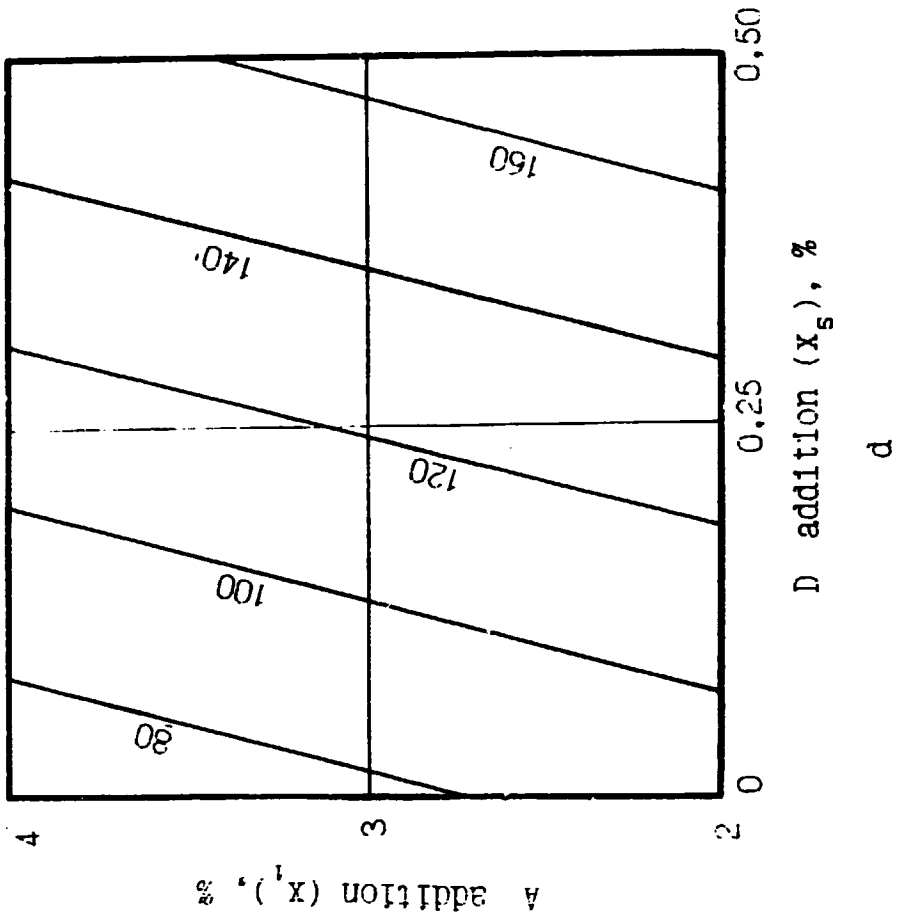
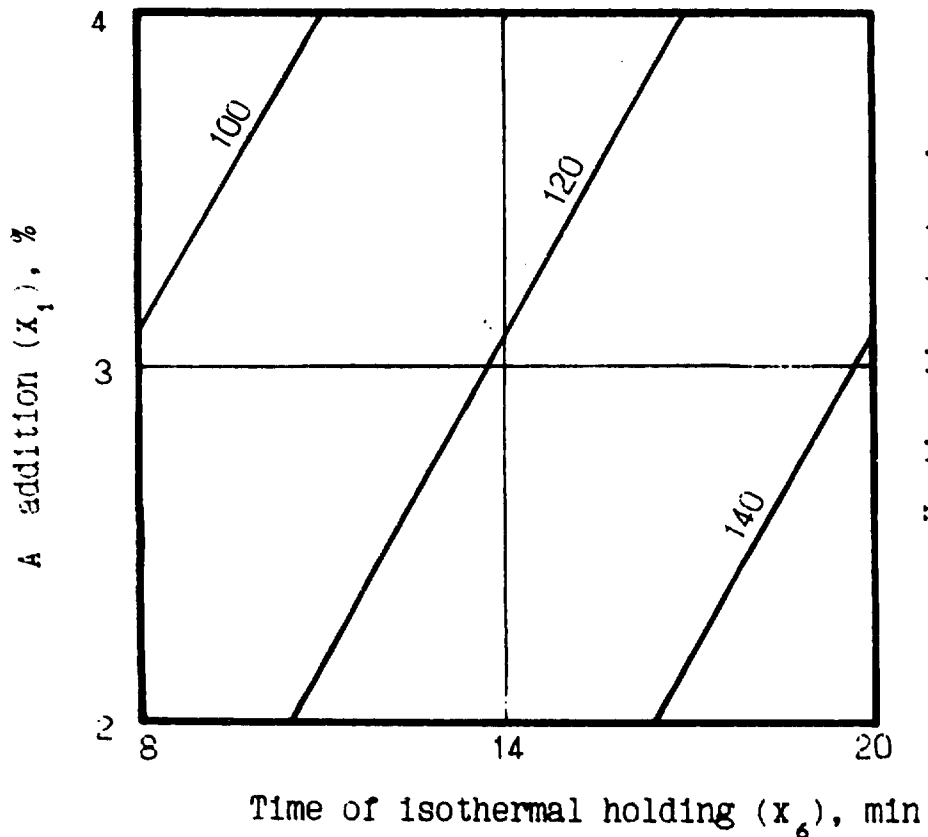


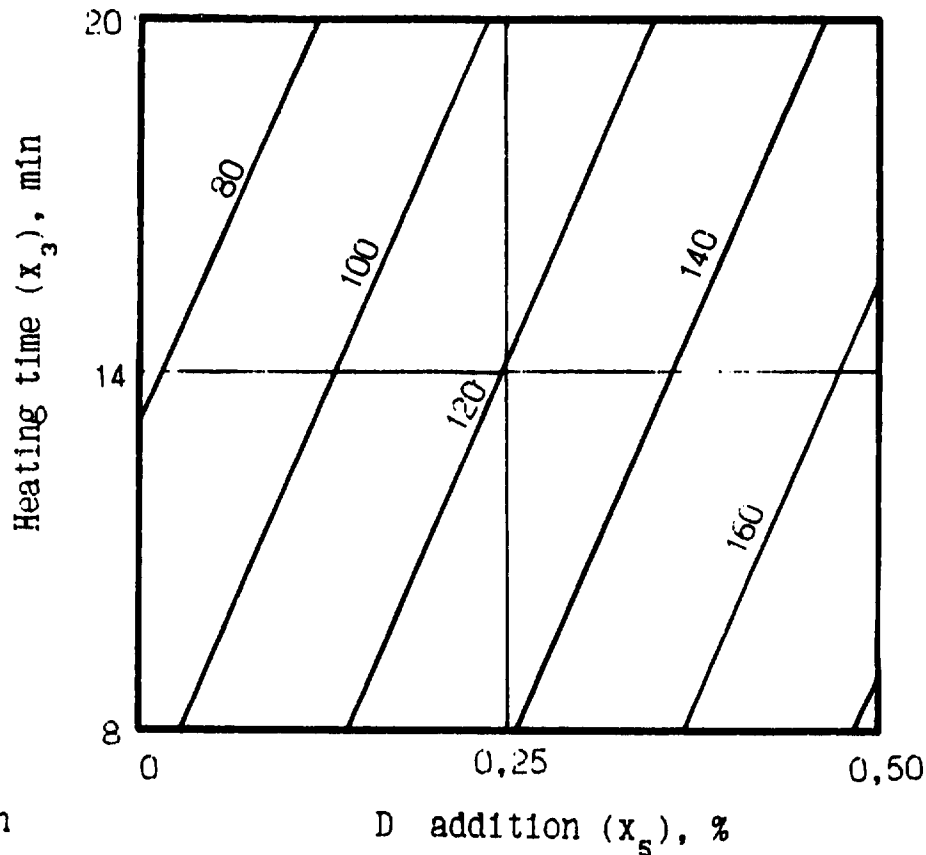
Fig. 4.1 Cont

$$y = 121 - 11x_1 + 20x_6$$



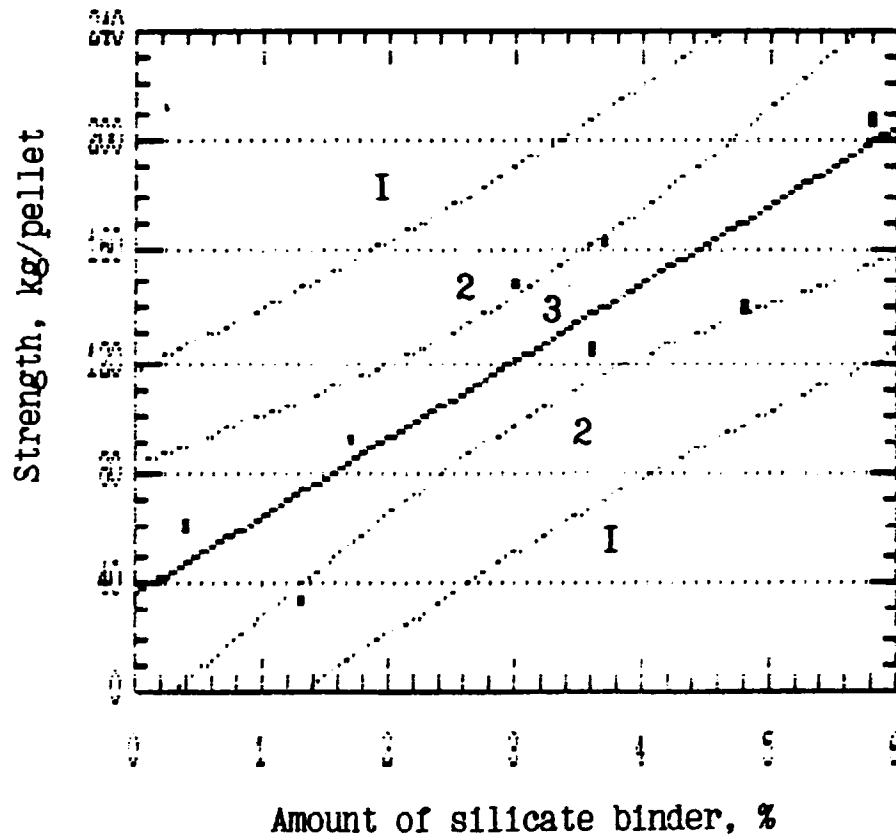
e

$$y = 121 - 18x_3 + 44x_5$$



f

Fig. 4.2. Dependence of the strength of roasted pellets on the amount of silicate binder



The graphs describe dependences of experimental data (dots) contained in Table 4.6. The data were processed by STATGRAPHICS program (Statistical Graphic System, version 2.0, Serial Number 295792).

Two extreme curves (1) determine the prediction limits with probability degree of 0.95. The next two curves (2) situated closer to the basic one determine the confidence limits with probability degree of 0.95. The basic line (3) is described by a regression equation $y = a + bx$.

Fig. 4.3. Dependence of the strength of roasted pellets on the average size of pores

Regression Analysis - Exponential model: $y = \exp(a+bx)$

Dependent variable: 140 33 92 61 308 125 independent variable: 89 64 81 74 82 96

Parameter	Estimate	Standard Error	T Value	Prob. Level
Intercept	0.942398	1.53822	0.612656	0.566894
Slope	0.0454766	0.0188945	2.40687	0.0611

Analysis of Variance

Source	Sum of Squares	Df	Mean Square	F-Ratio	Prob. Level
Model	1.3005519	1	1.3005519	5.7930134	.06110
Error	1.1225176	5	.2245035		

Total (Corr.) 2.4230696 6

Correlation Coefficient = 0.732624
Std. Error of Est. = 0.473818

R-squared = 53.67 percent

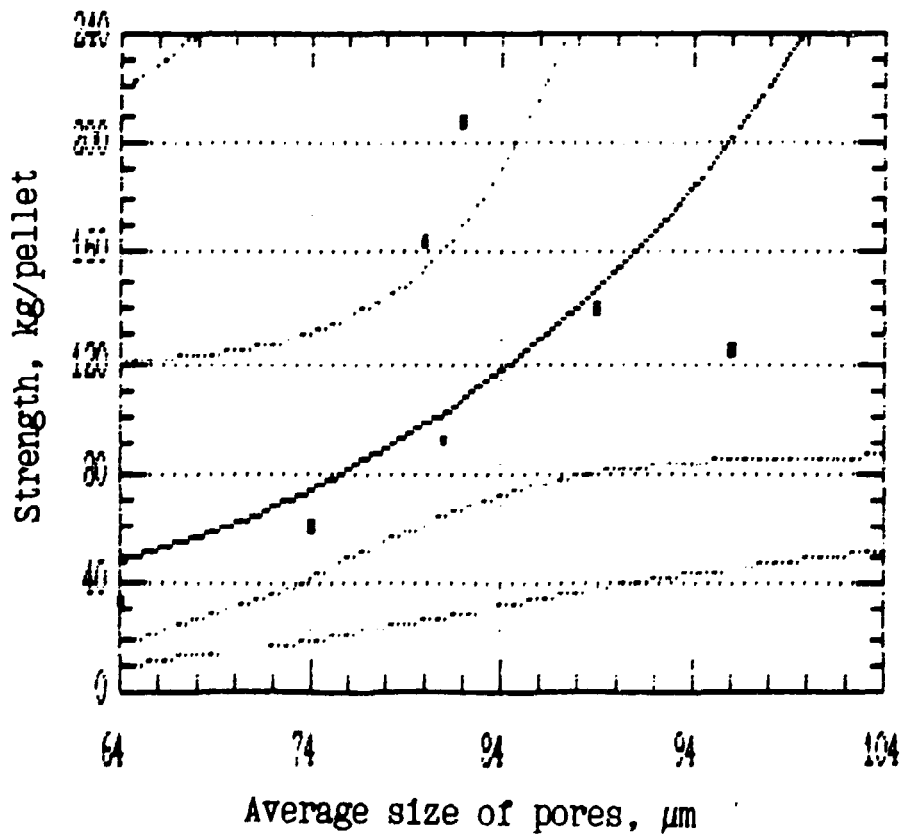


Fig. 4.4. Dependence of the strength of roasted pellets on the average size of intervals between pores

Regression Analysis - Linear model: $f = a+bx$

Dependent variable: 140 33 148 92 61 208 independent variable: 111 171 138 150 16

Parameter	Estimate	Standard Error	T Value	Prob. Level
Intercept	401.859	56.2394	7.14551	3.78674E-4
Slope	-2.07382	0.409871	-5.05968	2.3114E-3

Analysis of Variance

Source	Sum of Squares	Df	Mean Square	F-Ratio	Prob. Level
Model	18396.308	1	18396.308	25.600	.00231
Error	4311.5674	6	718.5946		

Total (Corr.) 22707.875 7

Correlation Coefficient = -0.900072
Std. Error of Est. = 26.8066

R-squared = 81.01 percent

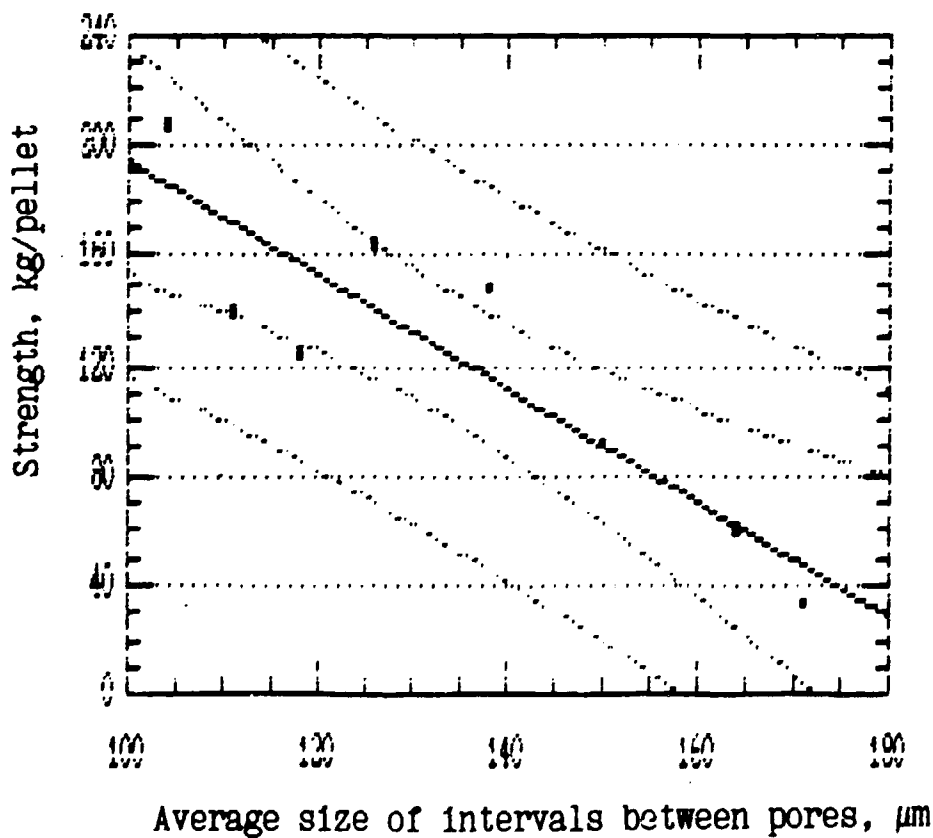


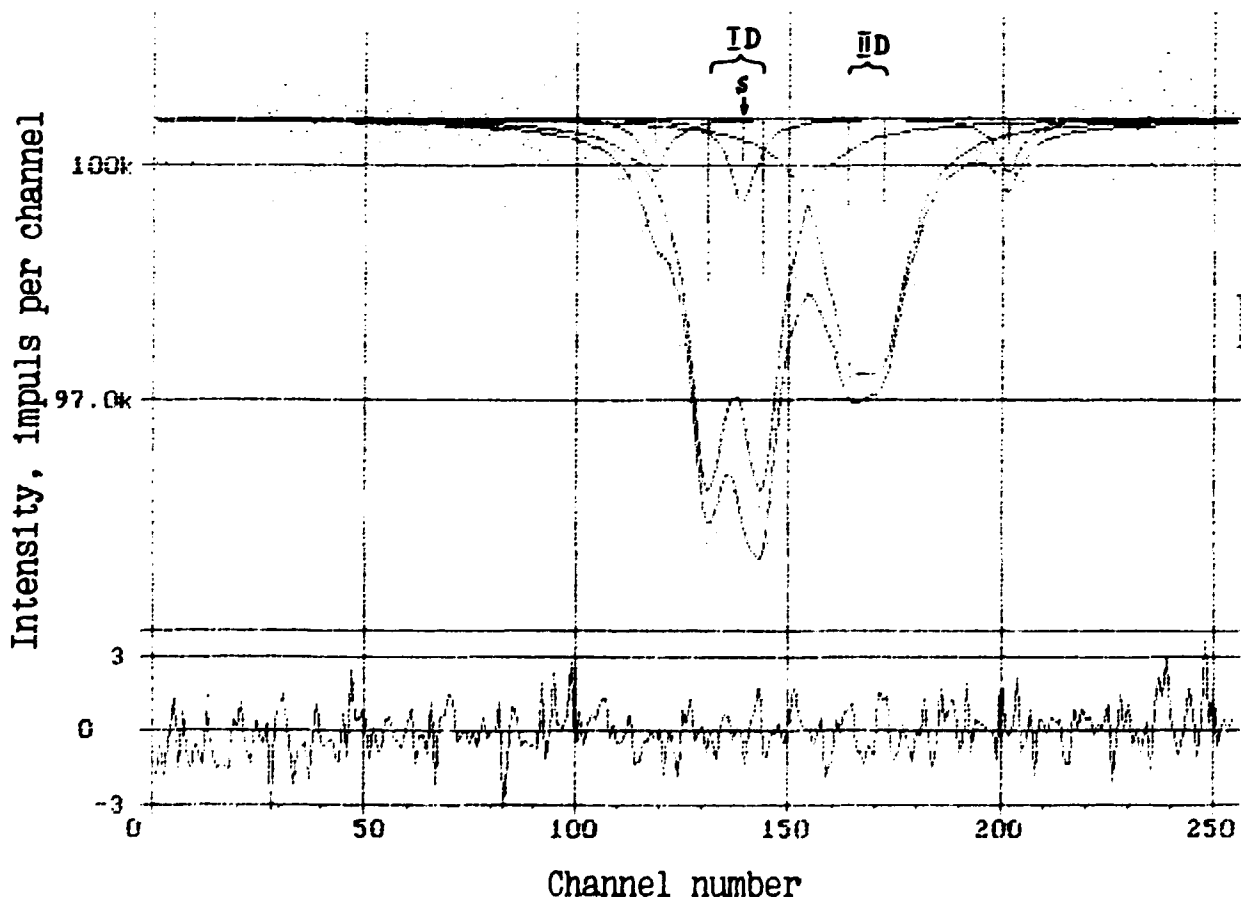
Fig. 4.5. Mossbauer absorption spectra for initial concentrate (a), check experiment (b), and test 6 (c)

g_line: 7 is (chan.)								
	a	err a	v	err v	g	err g	sq_line	err_sq_line
1	690	136	113.374	1.027	7.23	2.38	7720	1892
2	690	136	201.370	1.027	7.23	2.38	7720	1892
3	4146	143	130.802	0.316	11.02	0.72	71797	3381
4	4146	143	143.496	0.316	11.02	0.72	71797	3381
5	2249	148	163.551	0.520	14.29	1.47	50501	3919
6	2249	148	172.259	0.520	14.29	1.47	50501	3919
7	1166	438	136.924	0.791	7.10	4.94	12354	8295

is (ss/s)								
	a	err a	v	err v	g	err g	sq_line	err_sq_line
1	690	136	-0.036	0.036	0.25	0.08	0.002701	0.000662
2	690	136	2.985	0.036	0.25	0.08	0.002701	0.000662
3	4146	143	0.411	0.011	0.39	0.03	0.025116	0.001183
4	4146	143	0.848	0.011	0.39	0.03	0.025116	0.001183
5	2249	148	1.554	0.018	0.50	0.05	0.017666	0.001371
6	2249	148	1.860	0.018	0.50	0.05	0.017666	0.001371
7	1166	438	0.687	0.026	0.25	0.17	0.004322	0.002262

is %				
	a	err a	sq_line	err_sq_line
1	0.63	0.12	2.83	0.69
2	0.66	0.13	2.83	0.69
3	1.12	0.15	26.76	1.24
4	1.12	0.14	26.76	1.24
5	2.24	0.15	18.54	1.44
6	2.24	0.15	18.54	1.44
7	1.10	0.23	4.54	2.31

me_sp: B:\NALR\CHROM-1W.SPM
 tr_sp: chrom.concentr.rast.2.45



a

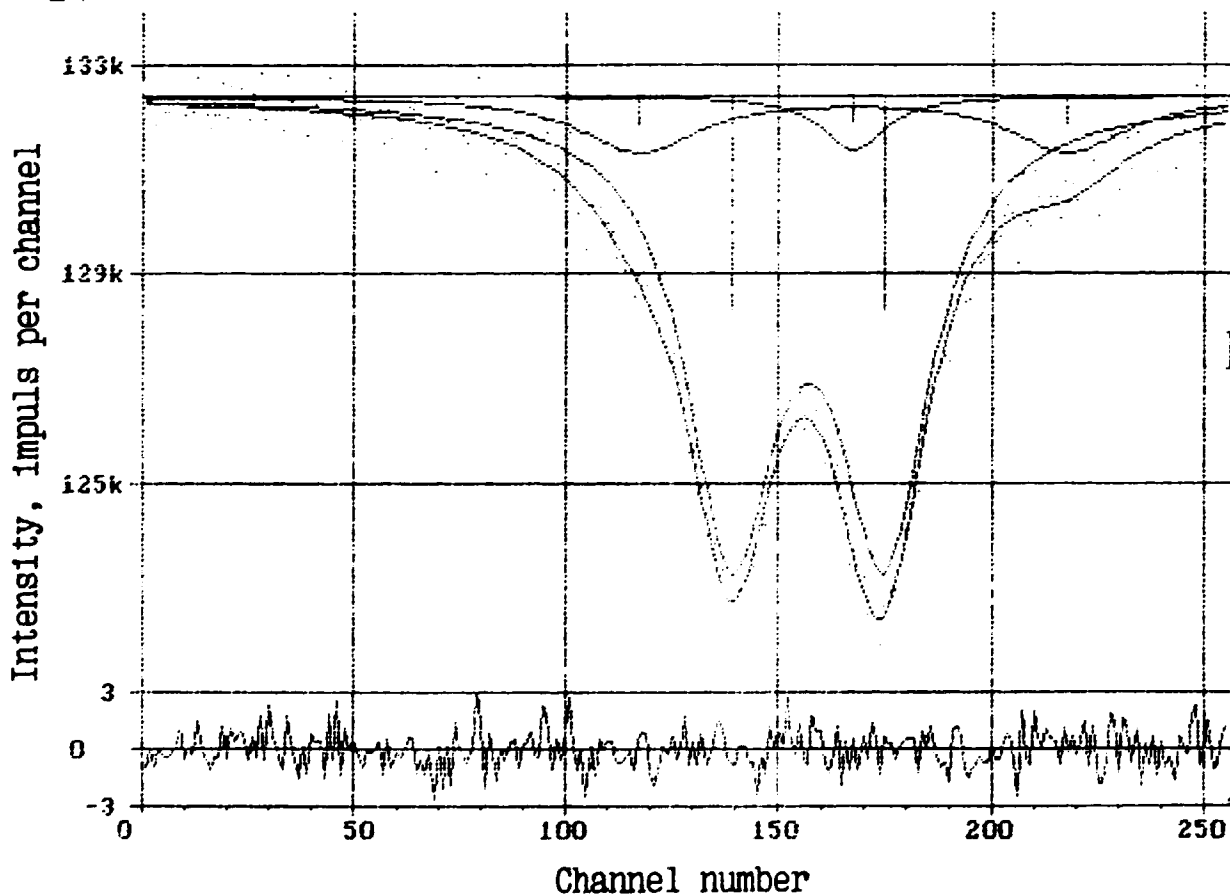
Fig. 4.5(cont)

g_line: 5								
in (chan.)								
j	a	err a	v	err v	g	err g	sq_line	err_sq_line
1	1050	99	117.147	1.976	33.44	0.21	55144	5392
2	1050	99	217.809	1.976	33.44	0.21	55144	5392
3	8214	140	138.870	0.247	25.64	0.67	330858	6587
4	8214	140	175.032	0.247	25.64	0.67	330858	6587
5	1028	226	167.467	1.968	18.00	0.00	29074	4067

in (cm/s)								
j	a	err a	v	err v	g	err g	sq_line	err_sq_line
1	1050	99	0.033	0.028	0.47	0.67	0.005877	0.000681
2	1050	99	1.453	0.028	0.47	0.67	0.005877	0.000681
3	8214	140	0.340	0.003	0.36	0.01	0.035260	0.000702
4	8214	140	0.850	0.003	0.36	0.01	0.035260	0.000702
5	1028	226	0.743	0.028	0.25	0.00	0.003099	0.000433

in %				
j	a	err a	sq_line	err_sq_line
1	0.79	0.07	6.88	0.80
2	0.79	0.07	6.88	0.80
3	6.20	0.11	41.30	0.82
4	6.20	0.11	41.30	0.82
5	0.76	0.17	3.63	0.51

me_sp: A:\ALB\CHROM-4.SPM
 mm_sp: chrom.ALB-control.in.



b

Fig. 4.5(cont)

a_line: 5
in_chan: 1

	a	err a	v	err v	g	err g	sq_line	err_sq_line
1	738	105	122.228	1.309	14.05	2.87	16294	2589
2	738	105	163.523	1.309	14.05	2.87	16294	2589
3	4426	169	129.304	0.197	9.79	0.48	68085	2699
4	4426	169	144.164	0.197	9.79	0.48	68085	2699
5	1308	255	141.269	0.581	6.00	6.16	12327	8200

in_chan: 1

	a	err a	v	err v	g	err g	sq_line	err_sq_line
1	738	105	0.099	0.046	0.49	0.10	0.008013	0.001269
2	738	105	1.555	0.046	0.49	0.10	0.008013	0.001269
3	4426	169	0.266	0.007	1.34	0.02	0.033424	0.001328
4	4426	169	0.371	0.007	0.34	0.02	0.033424	0.001328
5	1308	255	0.770	0.020	0.21	0.22	0.006663	0.004032

in_chan: 1

	a	err a	sq_line	err_sq_line
1	1.03	0.15	9.00	1.42
2	1.03	0.15	9.00	1.42
3	6.18	0.24	37.60	1.49
4	6.18	0.24	37.60	1.49
5	1.83	0.35	6.81	1.53

_sp: A:\ALB\CHROM-4M.SPM
_sp: chrom.ALB-6.rast 2.45.

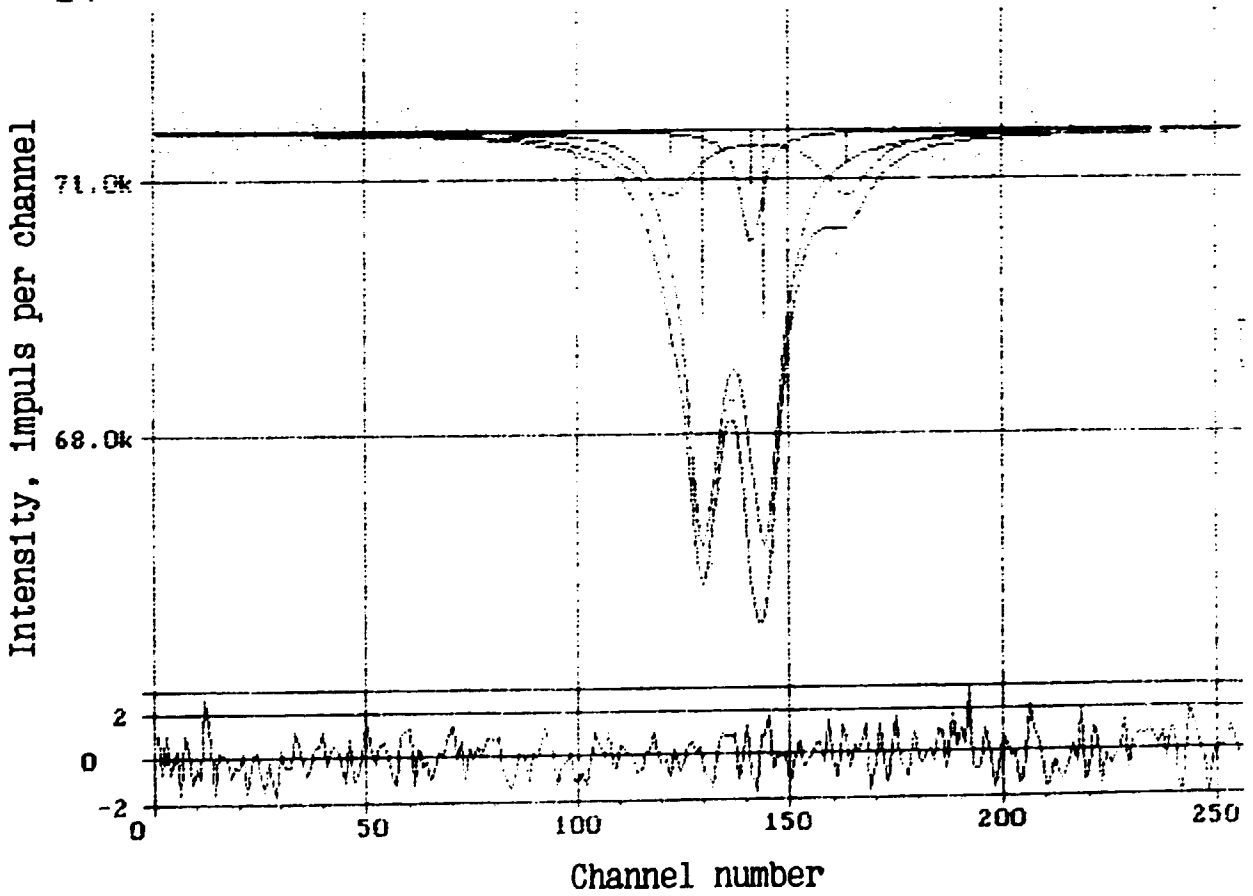


Photo 4.1. Texture of the Albanian chromium ore (x 300)



Photo 4.2. Microstructure of the Albanian chromium ore (x 500)



Photo 4.1. Microstructure of roasted pellets:
test 1 (a), test 8 (b)



a



b

white - chromespinelide
grey - binder
black - pores

Photo 4.4. Macrophotos of ore-fuel pellets and HPS-product

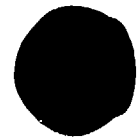


Figure 1. Scanning electron micrographs of fuel pellets and their products. The charges include different additions of HPS: a - pellet, b - HPS-product.



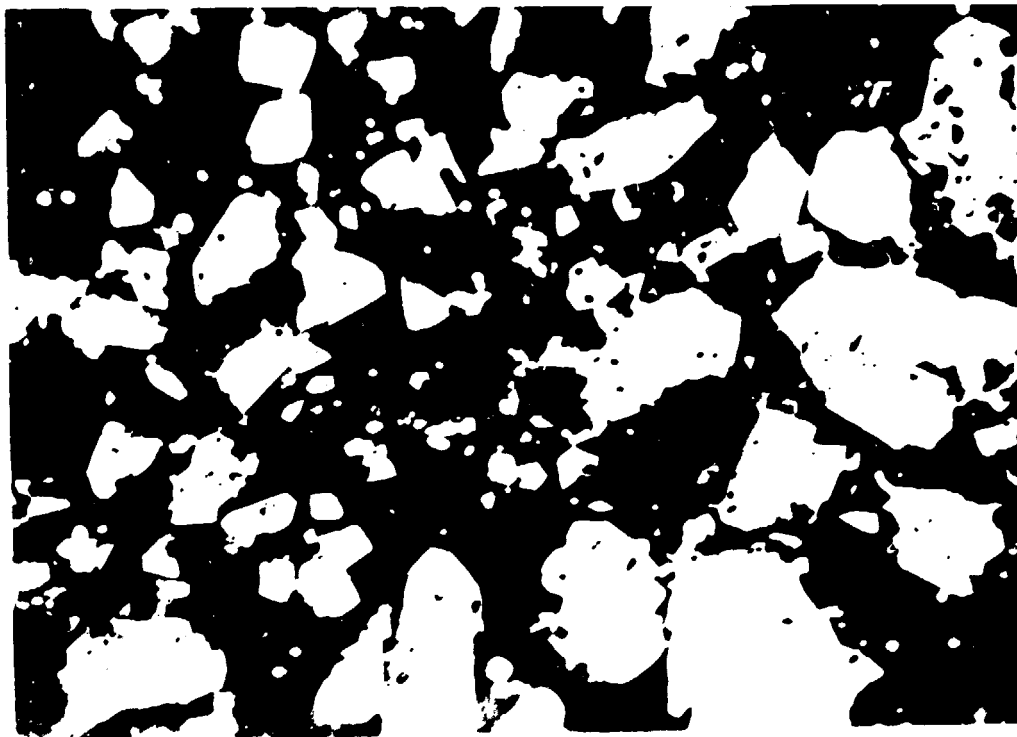
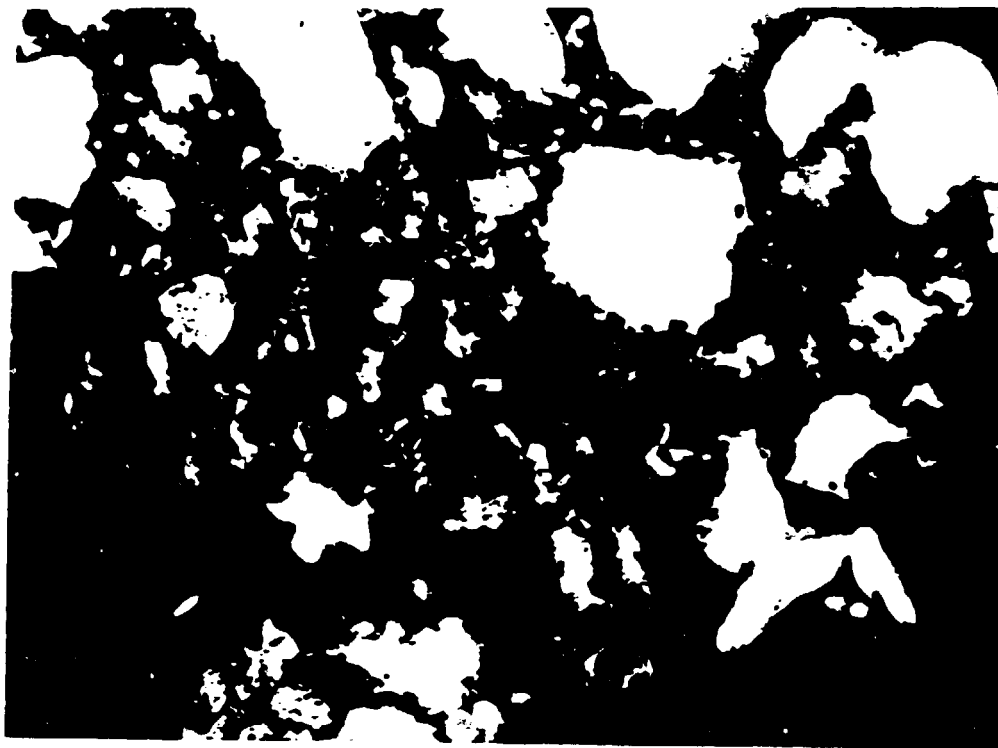
a



b

white	metallic phase	grey-black - silicate binder
white-grey	chromo-spinel-like	black - pores

Photo 4.5. Microphotos of microproduct of 1000
recharges include different additions!



5. SPECIFICATION OF THE COMPOSITION AND PROPERTIES OF SOURCE
MATERIALS AND THE PRODUCTS OF ALBANIAN CHROMIUM CONCENTRATE
AGGLOMERATION

Source materials

a) Concentrate.

The grain size is less than 0.1 mm ($\geq 95\%$); chemical composition is (weight percent): 47.0-50.0 Cr_2O_3 , 2.7-3.8 FeO, 7.0-9.0 SiO_2 , <20.0 MgO, <0.05 P, and <0.05 S.

The $\text{Cr}_2\text{O}_3/\text{FeO}$ ratio is 3.0-3.5, humidity is 6-10%.

b) Bentonite.

The grain size is less than 0.05 mm ($\geq 90\%$), swelling is not less than 12 times, humidity is 3-4%.

c) Solid fuel.

The kind of fuel is the know-how.

d) Additions A, B, C, D.

The kind of additions is the know-how.

Agglomerated products

a) Roasted pellets.

The size of pellets is 10-14 mm, compressive strength is 150-250 kg/pellet, chemical composition is practically determined by the composition of source concentrate.

b) HPS-product.

The size of lumps is 10-80 mm.

The strength of lumps makes it possible to transport them from a roasting machine to a ferroalloy furnace without visible crushing.

Unlike pellets, HPS-product contains 5.0-30.0% $(\text{Fe,Cr})_{\text{metal}}$ and up to 10.0% $(\text{Fe,Cr})_7\text{C}_3$.

6. PRELIMINARY DESIGN OF THE PROCESS FOR MAKING PELLETS OUT OF ALBANIAN CHROMIUM CONCENTRATES

6.1. A Flow-Sheet for Making Roasted Pellets and HPS-product

A technological chain for making pellets includes the following operations:

1. Crushing of the source materials (concentrates and additions) with further re-grinding down to the fraction of less than 0.1 mm.

2. Proportioning and mixing of the charge components.

3. Agglomeration (making 10-14mm diameter wet pellets) on a plate granulator, screening.

4. Charging of wet pellets on pallets of a roasting machine of the conveyor type. The height of the layer of pellets is 200-300 mm, not taking into account the height of the bottom bed.

5. Thermal treatment of pellets on a roasting machine:

- a) drying of pellets (150-400°C);

- b) heating (900-1200°C);

- c) roasting (1300-1350°C);

- d) recuperation (1100-1250°C), burning of gas in a layer;

- e) cooling down to 100°C.

6. Unloading of roasted pellets with further screening and the deposition of a part of pellets on the side and bottom beds.

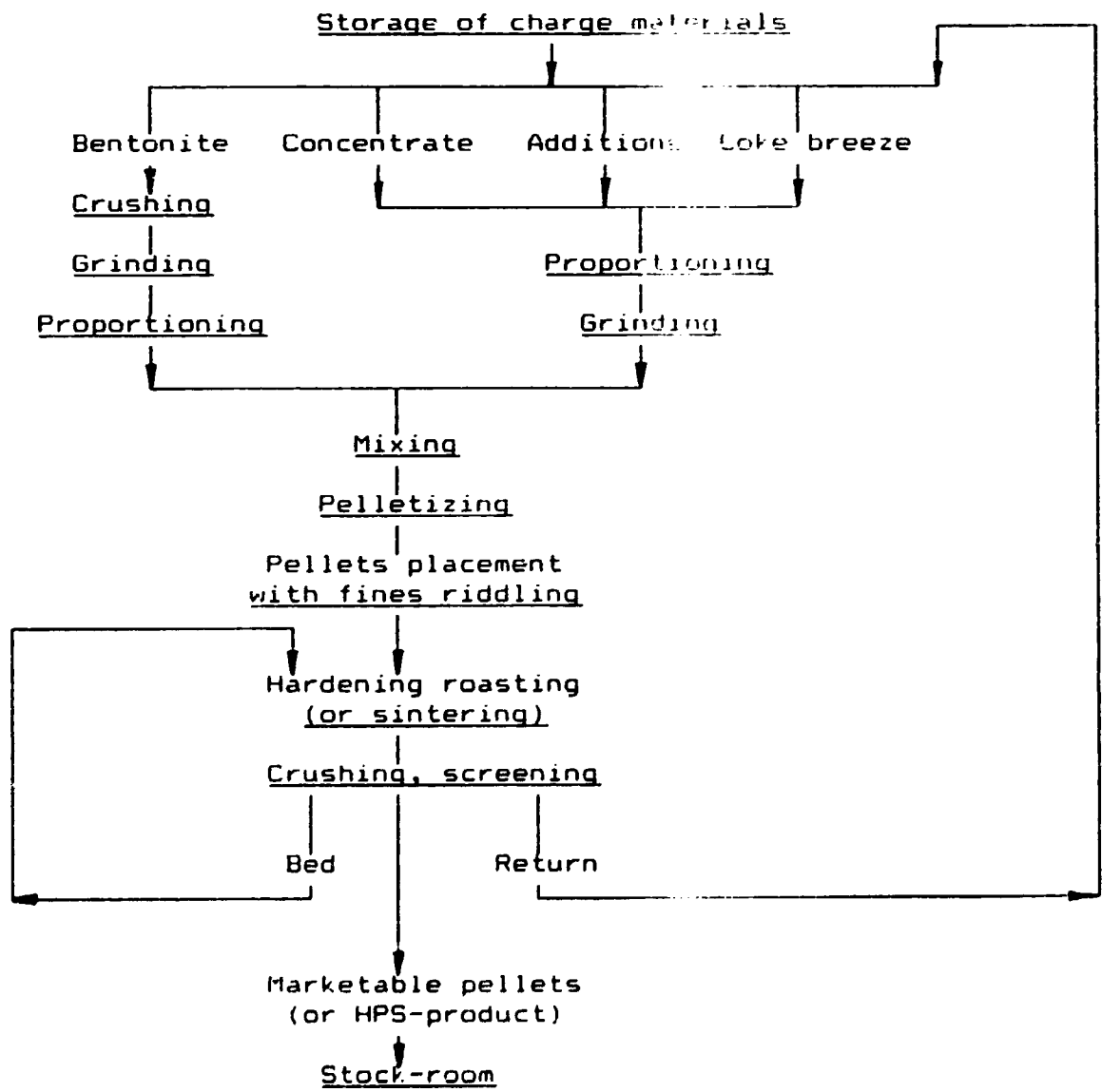
7. Transportation of pellets to a stock-room.

The process of making HPS-product differs from that of making roasted pellets in an existence of solid fuel in the charge introduced by different methods, in the size of wet pellets, in the

conditions of high-temperature hardening, and in the composition of gaseous phase.

An equipment for making HPS-product may be the same as for making pellets. For fast (operative) transition from making one agglomerated product to another (from pellets to HPS-product), it is desirable to use a universal roasting conveyor machine made by "Uralmash" (the know-how).

A Flow-Sheet for Roasting Cr-Bearing Materials



6.2. The Structure of the Agglomerating Plant, a List of Main Equipment and its Specification

The proposed agglomerating plant should contain the following components:

- input device,
- automated material store-house,
- a block for charge materials preparation and drying bay,
- a block for proportioning and pelletizing,
- roasting block,
- pellets loading hopper,
- automated store-house for finished pellets,
- a block for filtering and thickening of slime,
- administrative and servicing block with automated system for production process control,
- compressor house,
- pump houses with fire-prevention reservoir,
- boiler room.

Main Production Equipment

- Coke breeze crushing - Grinding complex (the know-how, "Mekhan-
obr")
- MTs Centrifugal mill, Q = 5 t/h (for a 0.074mm class)
- Hummer crusher
- Bentonite crushing - Grinding complex (2660x1770x1290mm holefull
rollers)
- Bentonite pre-drying - BN 2.2-10-NTs-03 drum drier

Material grinding	- Grinding complex (ball mills, cement mills)
Charge materials mixing	- Double-roller mixers (SMF-126) Disintegrator (V-800) rotor mixer)
Charge pelletizing	- Pelletizers - bowl (3200mm diameter), drum
Wet pellets placement	- Loading device ("Uralmash" roll placer)
Hardening roasting of pellets and their cooling on a machine down to 100°C	- 36 m ² (22 m ²) roasting machine
Sinter crushing	- Roll (jaw) crusher
Pellets screening	- GSB self-balance screen

The problems of air aspiration and lifting equipment have been solved for all the producing and service buildings and constructions.

Flexible control of the process and its parameters is achieved with the help of an automated control system with an output of the information on the functioning of both separate units and the plant on the whole onto a printer.

Slimes are utilized by an equipment with thickeners and filters located in the block of thickening and filtering.

Slimes are used in the process, clarified water is recycled.

The plant is for the most part ecologically clean and wasteless.

The layout of the agglomerating plant with the planned arrangement of main blocks is presented in Fig. 6.1.

6.3. Material and Energy Balances for the Process of Albanian Chromium Concentrate Agglomeration. Main Technical-And-Economic Indices

It has been assumed in preparing a material balance for pellets production that the weight changes in the process only due to moisture withdrawal and decomposition of hydrates (carbonates).

Material balance (kg/tonne of finished product)

Input	kg/tonne	%	Output	kg/tonne	%
Concentrate	1106	63.5	Pellets	1000	57.4
Bentonite	5	0.3	Fines (spilling)	70	4.0
Water	100	5.7	Bed recovery	20	1.2
Bottom bed	473	27.1	Transition to gaseous phase	120	6.9
Side bed	59	3.4	Bottom bed	474	27.2
Total:	1743	100.0	Side bed	59	3.4
			Total:	1743	100.0

Energy balance calculation requires experimental data which can be obtained only as a result of studying the process of layer roasting. This was not feasible at this stage of investigations owing to the absence of the required amount of concentrate (1 tonne). Therefore, like in the process of iron-ore pellets roasting, an approximate evaluation has been made of the expenses for making 1 tonne of roasted Cr-bearing pellets.

*Main technical-and-economic indices of pellets production
(approximately)*

1. Specific output of roasting machine, t/m ² ·h	0.5
2. Specific rate per one tonne of roasted pellets:	
a) electric power, kW·h	150-180 (for dry grinding)
b) compressed air, m ³	40
c) service water, m ³	15-20
d) natural gas, m ³	90
e) equivalent fuel, kg	105

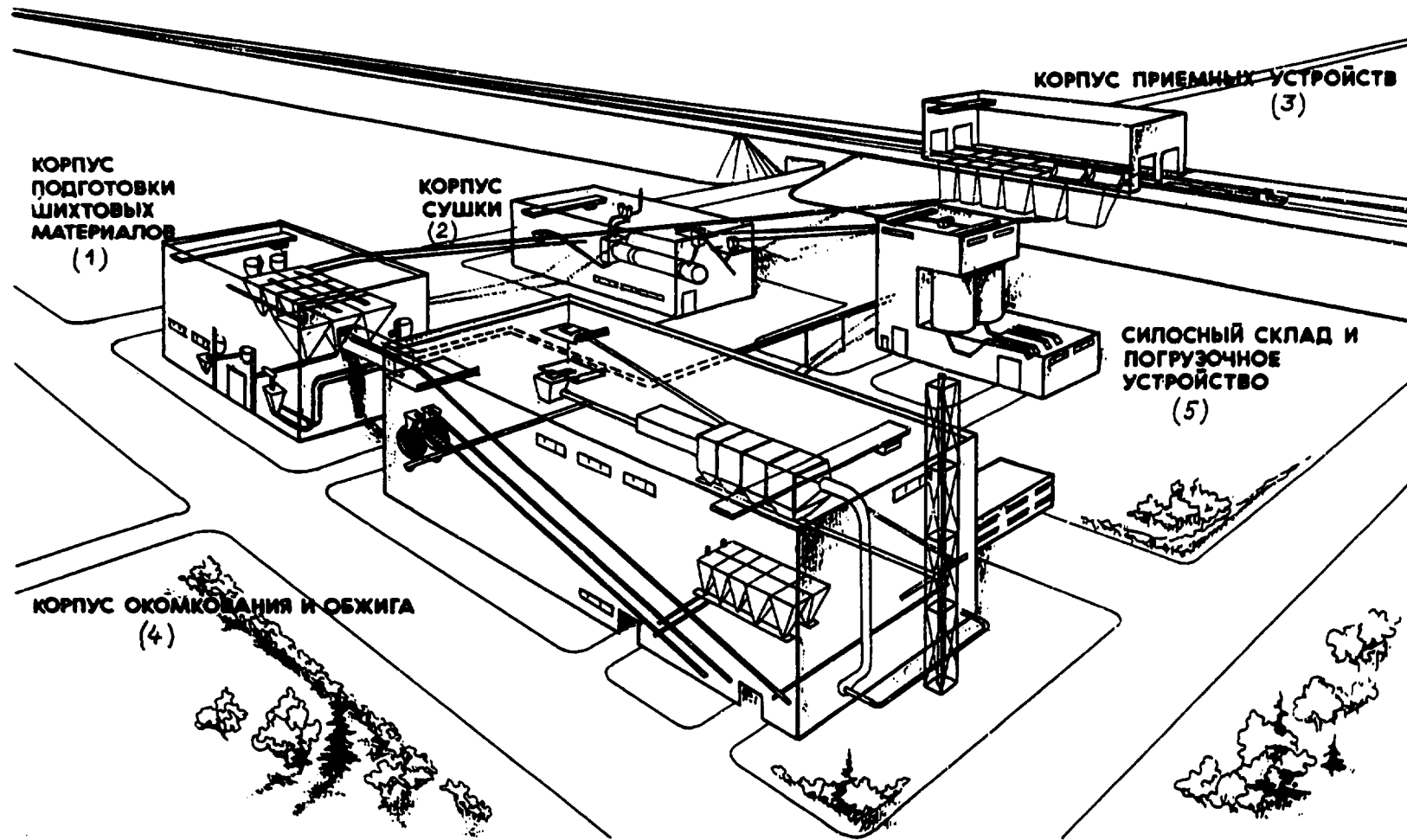


Fig. 6.1. Layout of the agglomeration plant:
 1 - block for charge materials preparation; 2 - drying block; 3 - block of input devices;
 4 - pelletizing and roasting block; 5 - silo storehouse and loading device.

7. CONCLUSIONS AND RECOMMENDATIONS

1. The study of the processes for the agglomeration of chromium ores and concentrates used in the world practice, as well as an experience of working in this field, make it possible to conclude that it is inexpedient to briquette Albanian chromium ores and concentrates both from technological and economic points of view. A method of making pellets with or without solid fuel addition and with further hardening roasting is the most promising.

2. The examination of Albanian chromium ores and concentrates has shown that their compositions vary considerably depending on their deposit. Taking into consideration the requirements to charge materials in making ferroalloys, it is possible to conclude that not all of the Albanian ores and concentrates could be directly used for making agglomerated raw material.

3. In order to produce agglomerated raw material with optimal composition and properties, it will be necessary to use a mixture of different ores (fines) and concentrates, as well as additions of natural minerals occurring in Albania and the waste of allied production. As the preliminary study conducted in MISA has shown, if there is a lack or absence of bentonite clays, it is possible to use stripping rocks (a by-product in mining chromium ores) as a binder.

However, during the feasibility study, it will be possible to select the conditions allowing to obtain agglomerated raw material without binders.

4. The results of the investigations conducted in MISA were sent for verifying an ability of making roasted pellets with sufficiently high strength and hybrid pelletized sinter (a HPS-product) after a preliminary design of an agglomeration flow-sheet, having Albanian chromium concentrate as a source material.

5. To verify an ability of making roasted pellets and HPS-product out of Albanian concentrates, a preliminary study has been conducted in MISA concerning the distinctive features of the mineralogical and phase compositions of Albanian chromium ores and concentrates as well as their pelletizing ability. The behavior of chromium concentrate during the process of heating and high-temperature roasting has been also studied.

6. As a result of the tests conducted, an ability is verified to make pellets out of Albanian chromium ores and concentrates with the strength allowing their transportation. It is achieved by the introduction of certain additions into the charge (the know-how).

However, pellets are inferior to lumpy ore in their properties (in particular, in their behavior in melted slag when used in high-carbon ferrochromium making). Therefore, it is expedient to use pellets made by the process suggested in the charge of ferroalloy furnaces in combination with lumpy ores, or for export.

The nomographs presented in the report are possible to use for operating the quality of pellets.

7. An ability of making HPS-product out of chromium ores and concentrates by the new process has been shown in laboratory conditions (the know-how).

Further crushing of HPS-product will make it possible to obtain lumps of the desired sizes (10-80 mm), which is very important for making high-carbon ferrochromium. The rate of dissolution of sinters in melted slag corresponding in its composition to that in high-carbon ferrochromium melting is comparable with the rate of dissolution of lumpy ore. It will permit to increase the production of ferrochromium in Albania by means of involving the concentrate and fines of chromium ores into the process.

The advantages of HPS-process, as compared with making pellets, is a possible decrease of energy expenditures for the process in the whole. This is achieved by the use of inexpensive kinds of solid fuel in the charge.

8. A flow-sheet for the process is designed with a list of main equipment.

It is planned to maintain two conveyor-type machines with baking area of 22 (36) m² each for roasting pellets at the future plant. After the process design, it would be possible to make HPS-product on one of these machines. The design of such universal machines has been prepared at "Uralmekhanobr"- "Uralsmash" Scientific Production Amalgamation. The output of the plant with two roasting machines in that case will be equal to 100,000-300,000 tonnes per year when working on two machines with baking area of 22m² each and 260,000-500,000 tonnes per year when working on machines with baking area of 36m².

An equipment for making pellets and HPS-product according to the processes suggested will not really differ from that used at pelletizing plants nowadays.

9. The flow-sheet, roasting conditions, and a list of main equipment presented in this report are draft. Their clarifications will be available after the feasibility study, including large-scale laboratory tests, and further design preparation.

10. The unit and equipment proposed in the report have demonstrated high ecological cleanliness and reliability. The aspiration system ensures air cleanliness at the working places. The content of NO_x and CO in waste gases is insignificant. Solid waste utilization is also provided. Water pollution does not take place.