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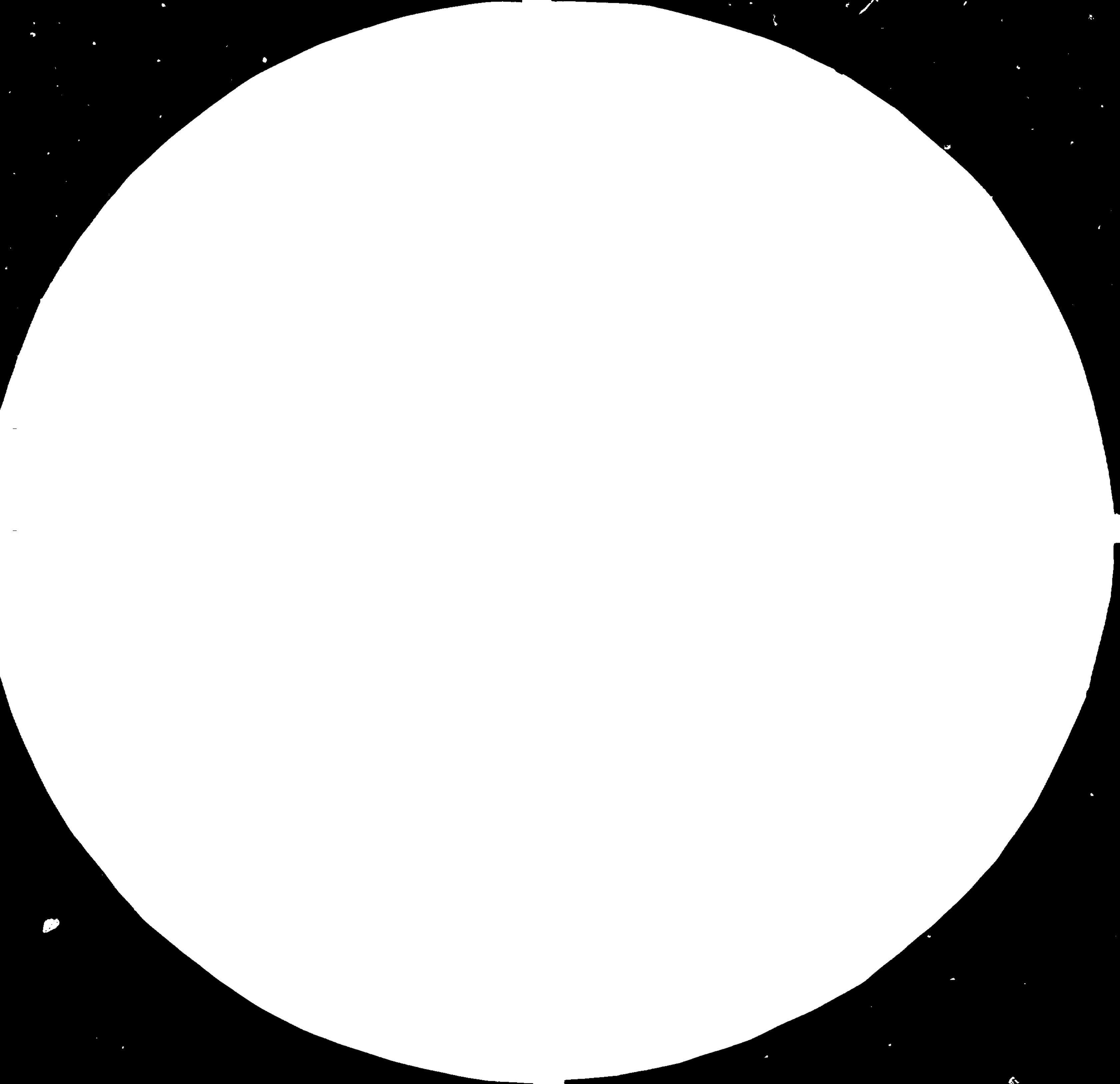

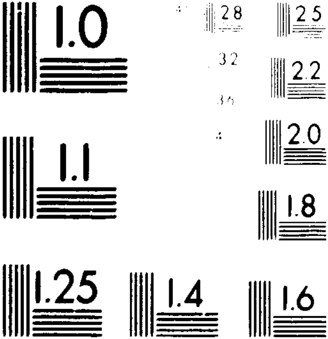
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INDUSTRIAL EXPLOITATION OF GRAPHITE

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ABSTRACT

This paper presents the fundamental information on graphite. It defines its properties, deals with the geology of graphite deposits and mining methods.

The chapter on graphite preparation deals with classical methods that are applicable only for minerals of high graphite content and easily removable waste. The most frequently used flotation method is described including physical principles and industrial application. The phase of graphite concentrate refinement is concerned with chemical refining methods and there industrial application.

Very informative is the review of application of graphite semifinished and finished products in various industries.

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INTRODUCTION

From the point of view of the national economy, graphite is a very important raw material finding use in many branches of human activities. People recognized it a long time ago. The importance of graphite has grown rapidly in modern times since the quickly developing industry required such a material very urgently. Nowadays graphite is often denoted as a strategic non-metallic raw material. Information concerning its mining is often considered as confidential and for this reason the accurate and reliable data about its annual production cannot be obtained. The importance of graphite during the contemporary era has grown especially due to the fact that this material serves in atomic power plants. It is known that the consumption of graphite for building an atomic power plant amounts approximately to 12.2 - 14.2 tons per 1 MW.

Since the application of atomic energy for the industrial and civil purposes seems to be an only way out from the energy shortage in many countries in the near future, it is obvious that the attribute "strategic" is not exaggerated in case of graphite.

The possibility of graphite export contributes to the sound development of each state economy. The UNIDO-Czechoslovakia Joint Programme issues this publication which ought to give the reader the basic information about the physico-chemical properties of graphite, about its natural resources, mining, refining and application in the most important branches of industry and in civil life at all.

I. GRAPHITE PROPERTIES

1. Chemical Properties

From the physico-chemical point of view, graphite is one of the allotropic modifications of carbon. Diamond crystallizes in a cubic crystal system whereas graphite in an hexagonal one. Both these modifications differ essentially from each other with respect to their physical and chemical properties. The discovery of the crystal structure of graphite belongs to the great merits of Debye and Scherrer who applied their own roentgenographic method for the solution of this difficult problem. The graphite crystal lattice is shown in Figure 1. In this hexagonal graphite lattice, each carbon atom has four valence electrons. Three of them form covalent bonds with neighbouring atoms. The fourth electron is bound much more loosely. The layers are formed by hexagonal rings held together by van der Waal`s forces. Adjacent atoms in any layer are closer than the spacing between layers. Such atomic configuration results in an extreme anisotropy. This anisotropy substantially affects the properties of all graphite forms. For example, thermal and electrical conductivity are high in the direction parallel to the planes formed by carbon atoms. The inverse effect is observed in case of thermal expansion. Graphite consists largely of ordered graphitic structure but it has been found that in many graphites as much as 15 per cent of matter is represented by disordered forms of carbon. This fact depends especially on the quality of raw materials and also on the maximum temperature of heating during fabrication. Well ordered and disordered forms of carbon are extreme cases and between them there is the whole continuum of various crystalline sizes and degrees of order.

Some other particles - atoms, ions or molecules - can penetrate between the layers into the graphite lattice. It represents certain analogy with hydrides, nitrides and carbides of some metals.

For example, if graphite is brought in contact with gaseous fluorine at the temperatures in the range 20 - 100°C, a process is initiated the result of which is the emergence of black powcer of composition from C_4F to C_3F_6. These compounds are stable enough not to enter into reaction with diluted acids and lyes. On heating above 100°C they decompose. The atomic configuration of C_4F does not differ too much from that of graphite. The only substantial difference consists in the fact that the corresponding carbon atoms in neighbouring layers are situated on line perpendicular to those layers and that between individual layers there are atoms of fluorine. Nevertheless, the fluorine atoms are imbeded always in two neighbouring layers, so that we must presuppose, that there is not mere mechanical imbeding here but rather a chemical process accompanied by the volume expansion of graphite. The distance of layers increases in this case from 3.35 Å to 5.5 Å. The properties of graphite are completely changed after the reaction with fluorine. E. g., its electrical conductivity is then only one per cent of the original one. In the temperature range 420 - 460°C, graphite reacts readily with fluorine to form the non-stechiometric compounds from $CF_{0,7}$ to CF. These compounds are also sufficiently stable. They do not react even with strong acids and lyes. The wide composition range of these compounds is in the correspondence with the course of changes in their properties. While $CF_{0,7}$ is a red compound, CF is quite colourless having practically no electrical conductance. Free electrons are obviously needed for the formation of the C - F covalent bond in this case. The distance between layers reaches 8.17 Å with the CF compound. On heating at the temperature above 500°C, the compound CF decomposes into "conventional" fluorides of graphite, such as CF_4, C_2F_6, etc.

Graphite can also absorb oxygen at certain conditions. The products of this reaction are called graphite oxides. They can be prepared from graphite by means of the effect of strong oxidizers, such as KM_nO_4, $KClO_3$, or the mixture of H_2SO_4 and HNO_3. These reactions are also accompanied by changes in colour. Black graphite becomes gradually brown, green, yellow and in the end converts into the colourless compound with low electric conductivity. These graphite oxides can absorb molecules of water and some organic compounds (acetone, alcohols) and increase their volume during this process.

Different compounds have been prepared by the reaction of alkali metals with graphite in recent years. The products of reactions of $FeCl_3$ with graphite have been studied comprehensively.

As the result of these reactions, it has been recognized that the changes in crystal structure differ in individual cases. In some cases only the increase of the distance between layers in graphite crystal lattice is observed, sometimes the shift of the layers takes place accompanied even by their deformation.

In general, graphite is chemically very stable. Beside its interstitial compounds mentioned above, graphite forms compounds with molten metals. In this way different carbides can be prepared. Considerable practical importance have WC, TiC, CaC_2, SiC and B_4C which of course are prepared largely by some other types of reactions. Graphite can be burnt in the oxy-hydrogen flame and the formation of gaseous CO_2 and ash takes place. The quantity of ash can reach 20 per cent wt. here according to the graphite purity.

2. Physical Properties

All kinds of natural graphite are of black or dark grey colour and have an opaque character because they do not transmit light beams even in thin layers. The density of graphite is in the range 2.17 - 2.30. It possesses a metallic gloss. It is not hard, its hardness amounts usually to 0.5 - 1 according to Mohs. Cleavage is excellent in the bottom plane direction. Graphite shows both good electrical and thermal conductivity. Its purity has positive effect on these properties. Electrical conductivity of pure graphite is 2.5 times higher than that of mercury. Thermal conductivity reaches nearly the same value as platinum. The melting point is in the range 3 845 - 3890°C under the pressures from 0.1 to 1 MPa.

Graphite raw materials are classified mainly according to the size of particles. From this point of view graphite is divided usually into three groups as follows:

1/ coarse flake graphite
2/ fine flake graphite
3/ amorphous graphite

The most appreciated are the raw materials of macrocrystalline flake graphite. They can be utilized even in case of a low carbon content /5 - 6% wt. of C/. Raw materials containing finer graphite flakes show often considerable carbon content /e.g. 60 - 70% wt./ Amorphous natural graphites have their carbon content even higher /e.g. 70 - 80% wt. or more/.

3. Artificial Graphite

The industrial consumption of graphite has grown with considerable rapidity already in 19th century. For this reason, attempts were made to manufacture this material synthetically. It was Despretz who managed to prepare artificial graphite first. But this discovery remained unnoticed by the industrial circles in those times. Independently on this discovery, the preparation of artificial graphite was rediscovered later by Acheson.

Acheson tried to work out the technology of SiC for grinding purposes and reached this above-mentioned result obviously by chance. For the preparation of SiC, Acheson utilized the reaction

$$SiO_2 + 2\ C + 539\ kJ = SiC + 2\ CO$$

which was accomplished in an electrical resistance furnace. During the experimental work, an interesting fact was found. SiC appears as the main product of the reaction only in certain temperature range. On exceeding this temperature range, coarse flake graphite came into the existence. Later this discovery was used for the industrial production of artificial graphite. For this purpose, a special electric furnace was built in which higher temperatures could be reached. This high temperature furnace was filled by the mixture of quartz sand and coke and heated up to 3 000 °C. The reaction takes place here in several phases. At the beginning, SiC is also formed but it decomposes into coarse flake graphite. Silicium which is present in the reaction mixture has rather the role of catalyst here. Despite the fact that great quantities of graphite have been produced in this way, the mechanism of reactions is not completely known so far.

Almost any organic materials that leave a high carbon residue after heating can be used as raw materials in graphite manufacture. Because of their influence on microstructure and hence on properties, careful selection of raw materials is required to achieve the desired properties. A major source of raw materials for the manufacture of artificial graphite is petroleum coke, a refinery by-product from cracking of crude oil. Petroleum cokes are relatively cheap and usually free from impurities so that they are suitable for this purpose. Artificial graphites exhibit frequently greater purity than the natural ones containing 98 - 99.5 wt. of carbon.

To the family of artificial graphites, so called blast furnace graphite also belongs, arising during cast iron melting. Together with slag, it appears on the surface of the melt. There are methods enabling the separation of graphite from the slag by means of flotation. In comparison with natural graphite, this type of graphite contains some more of iron. Besides, this graphite arises, for example, during the manufacture of $CaCl_2$ and of aluminium from cryolith by means of electrolysis.

There is one process in the industrial practice which has certain relation to the manufacture of artificial graphite according to Acheson. It is so called graphitization which substantially improves the quality of refractory carbonaceous products made mostly from petroleum coke and coal-tar pitch as a binder, changing the crystal structure of amorphous types of graphite. This process consists in heating the products at the temperature about 2 500 °C in the reducing atmosphere. This heating is usually carried out in electric resistance furnaces and the consumption of electric energy amounts to 3 000 - 5 000 kWh/ton.

II. GEOLOGY OF GRAPHITE DEPOSITS

1. Geology of Graphite

As mentioned above, natural graphite has two main forms:

a/ macrocrystalline /e.g. flakes, plates, fibres/

b/ microcrystalline /"amorphous", represented by compact substance formed by small flakes of submicroscopic size/.

There are several theories concerning the formation of graphite in nature. Some experts are convinced that the origin of natural graphite is organic one, the others hold the opposite view. In general, it can be said that five following types of graphite deposits are found all over the world:

a/ deposits in basic and ultrabasic rocks

Graphite in this type of deposits is in the form of flakes and is probably of inorganic nature. Such deposits can be found in basalts or meteorites and have no importance for mining.

b/ deposits in pegmatites

Graphite is also in the form of flakes or radial aggregates here and its origin is probably inorganic,as well. These deposits are placed usually in the bodies of irregular shapes and exist for example in South Wales and Quebec /Canada/.

c/ migration deposits /assimilation deposits/

Graphites in these deposits are in the form of flakes and their genesis was probably as follows: rocks with high carbon or perhaps calcite content underwent the contact metamorphism.

Graphite is found frequently in veins imbeded in igneous rocks. These deposits exhibit nearly always a considerable quality (e.g. in Ceylon or East Sibiria/.

d/ kathametamorphic deposits

They contain usually flake graphites of the organic origin and impregnate frequently gneisses of different sorts. They came into existence by means of regional metamorphism of rocks having the high carbon content. The classical types of such deposits are in southwestern Czechoslovakia, Bavaria and Madagascar.

e/ epimetamorphic and contact deposits

They include only amorphous graphite imbeded in calcites and slates. The shapes of deposits are mostly irregular and in the form of seams. The origin of such deposits is obviously organic one. They were probably formed by the metamorphism of coal seams and calcites or slates.

To summarize, graphite is found either in igneous rocks or in metamorphous slates. The graphite deposits can have arbitrary shapes, irregular nests, lenticular bodies, seams, veins. But there might be some ingredients in the waste rocks causing difficulties during the graphite preparation. The worst impurities are represented by mica, chlorite and pyrite. Especially mica due to its physico-chemical properties can be separated from graphite only with peculiar difficulties. The content of graphite in its raw materials varies from 3 - 5% to 95 - 98% wt. Whilst rich graphites are usually found in thin veins, the deposits of low graphite content are often very large.

In the economic feasibility studies concerning the possibilities of mining graphite in particular place, all important factors must be taken into consideration: climate, transport, labour, carbon content, extent of the deposit and the composition of waste rock.

2. Deposit Prospecting

Most deposits have been discovered by chance, e.g. by the erosion effect of rivers during floods or on cutting down the trees. The deposits of graphite are frequently very irregular with respect to the spatial location. Therefore, the method of deep holes is not mostly suitable for their evaluation. Better way of prospecting consists in making the trenches and pits. It can be said that the graphite deposit prospecting is a very difficult task and that there is always the possibility of error. Recently introduced method of spontaneous polarization is to be advantagenous for the purpose mentioned above. It is based on the measurement of the intensity of electric fields arising in the rocks. If rock is sufficiently wet, different electrochemical process are under way. The existence of these electrochemical reactions is accompanied by the changes of electrochemical potentials. In case of graphite, such phenomena can be traced, for example, if diluted H_2SO_4 formed by weathering of pyrites is present. The presence of amphibolites in the nearness of deposits deteriorates the possibility of the application of this method. The results of such measurements must be checked by means of classical methods.

III. MINING

Different kinds of graphite deposits require the appropriate choice of mining method. Beside that the way of mining is dependent on the requirements of the preparation plant. There are two substantially different methods of mining: surface mining and deep mining.

1. Surface Mining

When graphite lenticular deposit, seam or vein is near the surface, surface mining is utilized. In Figure 2, the cross-section of Zettlitz mine (Austria) is shown. The deposit in Zettlitz is about 1 km long and some 22 m thick and is imbeded in the gently dipping slope underthe thin overlying sheet formed by weathered rocks. The mining is accomplished in several working faces having the height of 25 m. The faces are broken by pneumatic picks or sometimes by explosive blasting. Hand sorting and sizing of broken graphite raw material takes place on the spot. Then the material is transported to further treatment. Graphite from Zettlitz is also used in the blast furnaces instead of coke in case of the basic iron ore melting.

2. Deep Mining

When we cannot manage to hoist graphite by means of surface mining, deep mining must be applied. According to local conditions, different methods of deep mining are chosen. Two typical examples taken from Czechoslovakia are shown in Figures 3 and 4. Pneumatic picks and explosives are used here for exploitation. Broken material is sorted by manual work and transported by cars. Waste rock is either maintained in the exploited space or is transported to the dump on the surface.

The main obstacle with respect to the intensification of the production in case of deep mining is the necessary sorting of broken material and often the small size of the deposit.

IV. GRAPHITE PREPARATION

1. Classical Methods of Graphite Preparation

The preparation of graphite is a very complex process and it must be emphasized that the methods suitable for the preparation of the raw material from certain deposit cannot be always successfully used in other cases.

The simplest sorting of the waste can be chosen only in case of the materials with a high graphite content and easily removable waste. To tell the truth, such deposits probably do not exist in our times at all. Therefore, it is necessary to apply the more complex methods for this purpose. It is very important not to dammage the graphite flakes during the preparation.

The most delicate aspects of the preparation process are crushing and especially grinding of the graphitic raw material. For crushing the hammer crushers or certain kinds of impact pulverizers are successfully used. Some producers use also ordinary jaw crushers for medium or coarse crushing but there are often some operational difficulties in this case.

For fine grinding, a careful application of pan or ball mills is usually suitable. Nowadays, ball mills are preferred to other types of mills for this purpose. Ball mills have a good efficiency and can be better applied in continuous manufacturing processes but the quality of grinding is not in average as high as in case of pan mills. There is a danger that the material will be ground too much which is then the substantial obstacle during flotation process. For this reason, it is necessary to control the ball charge operating ball speed, etc. In general, it is advisable to experiment with respect to the way of crushing or grinding of particular raw materials.

Graphite pulp from the pan or ball mill is then washed. Washing of graphite pulp is carried out in the system of washing throughs where the fine sand settling occurs. Graphite settling takes place then in the sedimentation tanks. Coarse particles settle first, of course, then come finer ones. Settled graphite is dewatered in the press filters and then dried in appropriate driers.

There are also small portions of pyrite in some sorts of washed graphite. Pyrite must be removed on the vibratory tables introduced before the own washing.

2. Flotation

The most frequently used method for the graphite preparation is flotation. The first patent concerning the flotation process was granted just for the case of graphite in 1877. This procedure is really suitable for graphite preparation but only in the initial stages of the whole process. It is dependent on the manifold of factors like the crystal size, texture, admixtures, etc.

Nowadays, only in Ceylon there is a possibility to exploit the deposits directly and without further preparation. All other graphites with a carbon content over 90% wt. have been prepared by means of special treatments, mainly by flotation. We can say that it is especially flotation which enables us to make full use of the more inferior deposits of graphite. The content of the patent granted by Bessel brothers was as follows: to graphite suspended in water, some suitable organic compounds, carbonates and acids should be added during heating. The addition of 1 kg of chalk per 100 kg of graphite was recommended. The effect of acids on carbonates causes the evolution of gaseous CO_2 which results in forming the flotation foam. As organic compounds the portion of which was maximally

10% wt. in the suspension, different animal and vegetable fats, aetheric oils, kerosene, gasoline, paraffin, waxes, ozocerite, etc. have been used.

a/ Physical principles of the graphite flotation

Graphite belongs to the non-polar materials such as sulphur or carbon. Such substances show typical covalent bond in their atomic structure. This non-polarity results in their hydrophoby or water-repelling. Flotation of such materials takes place easily and often only foaming agents (without collectors) are necessary for its accomplishment. Such property of materials is called natural hydrophoby. Whilst waste rock is hydrophylic, i.e. water receptive, the graphite particles are not wettable. Just this fact determines the possibility of the application of flotation technique to the refinement of graphite.

Organic paraffinic oils added to the graphite suspensions are absorbed by graphite and increase its natural hydrophoby. They are called collectors. Since graphite is a hydrophobic material, the vertical component of surface tension acts here against the gravity vectors of the individual graphite particles. In this way the particles can be lifted to the surface of liquid. In case of hydrophylic mineral, the effect of surface tension is quite reverse. On the other hand, the foaming agents decreases the surface tension of water and must be, therefore, soluble in water to a certain extent. They create relatively stable foam on the surface of the pulp and support the absorption of gaseous phase by the individual particles causing at the same time decrease of their unit weight. The foaming agents are mostly represented by heteropolar substances the molecules of which comprise both hydrophobic and hydrophylic groups. Nowadays pine-oil, synthetic terpenylalcohol and xylenol are largely used for this purpose. The polar groups in the foaming agents have a strong affinity to molecules of H_2O. On the other hand, non-polar groups in these agents are oriented to gaseous phase, i.e. to the centres of air bubbles. In this way the air bubbles are protected against fusion.

Electric repulsion forces inhibit the development of big bubbles which are harmful to the whole flotation process and contribute to the stability of foam.

b/ Practical aspects of the flotation techniques

Flotation of the flake graphites is mostly easy. Its sensitivity to the changes of important technological parameters is negligible. Practically the only factor which has negative influence on the course of flotation in this case is the change of the raw material composition especially that of the waste rock or of clay minerals. This factor appears very often in practice and results in deterioration of the concentrate quality and in increase of carbon content in the process waste.

According to earlier notions, flotation of microcrystalline graphites (or so called amorphous graphites) is impossible. It must be conceded that considerable progress has been reached in this respect. At present, special firms flotate even these graphites in a quite satisfactory manner.

A decisive role in flotation plays the size and shape of graphite crystals. The main requirement here is to maintain the original size of the flakes during grinding. Only wet grinding is used for the disintegration of the graphite raw materials. By this wet grinding the disintegration of flakes is attained and at the same time the waste rock is separated from graphite. The preparation of graphite by means of the flotation is carried out in several stages. One stage consists in grinding operation and subsequent flotation. When the raw material passes through several stages, we can receive concentrates with carbon content reaching 94% wt.

In general, the preparation of graphite is unusually a difficult and complex process. Graphites with a carbon content over 94% wt. must be prepared by means of chemical refining.

Several flotàtion systems suitable for the preparation of graphite are shown in Figure 6. These systems have more stages. The systems in Figure 6 a/, c/, d/ have 4 stages, Figure 6 b/ shows three-stage system. These are many types of flotation systems for graphite preparation. The wastes from the individual stages are for example mixed together or returned to previous stages, etc.

Existence of the variety of different technological solutions in case of graphite preparation is determined or at least conditioned by the immense variety of the graphite raw materials with respect to their composition and texture. Frequently it is necessary in practice to prepare graphite from the deposit including both the flake and amorphous graphite. Such cases are most difficult to solve.

Despite the fact that flake graphite can be relatively easily flotated, amorphous graphites, on the other hand, require less case during grinding since the damage to crystals is not so dangerous here. It is then advisable to attain the disintegration of crystals as quickly as possible for example in one-stage system or maximally in two stages.

The industrial flotation processes are accomplished in many types of flotation cells or in hydrocyclones. The detailed description of these equipments can be found in special publications.

Flotation concentrates must be dewatered. For this purpose the filter presses are commonly used in Czechoslovakia. In other countries, vacuum filters or centrifugal separators are preferred. Filter presses are suitable especially for the dewatering of amorphous graphites. On the other hand, vacuum filters and centrifugal separators are commonly used for dewatering of flake graphites.

Graphite contains some 30% wt. of water after filtering and, therefore, it must be dried. In earlier times an open air drying has been frequently used. This way of drying is rather time consuming, little efficient and dependent on weather. At present time, rotary drum kilns are usually applied for drying. They are equipped by indirect heating and as fuel either coal or oil is used here. Also spray drying without filter presses has been successfully introduced in many cases. After drying the sizing of graphite according to the dimension of flakes must be accomplished. This sizing contributes to further purification and of course enables us to separate the individual fractions of graphite with respect to its practical application and price as well. The bigger and cleaner the graphite flakes, the greater their carbon content and also their price. The sizing of graphite is carried out by two different processes - on sieves or in the air flow. In the first process different types of sifters are frequently used. Air sizers introduced into the preparation of graphite later are reliable but more expensive.

V. REFINEMENT OF GRAPHITE CONCENTRATES BY MEANS OF CHEMICAL METHODS

Graphites with the carbon content over 94% wt. must be prepared chemically. Chemical methods of refinement find wide use if high purity of graphite is required and at the same time natural raw materials represent the point of departure in manufacturing process. From the historical point of view, methods of chemical refinement of graphite are older than those of flotation. In the times when manufacture of synthetic graphite was unknown and flotation undeveloped, chemical refining methods represented the only way to meet the sophisticated requirements of the contemporary producers. Nowadays, chemical refinement methods regain their position among graphite manufacturers especially due to the fact that pure graphite is the necessary mean for the atomic energy power plants and for certain branches of the chemical industry.

Schlaeffel method consists in leaching graphite by HCl and NaOH, subsequent melting with soda and washing by warm water. Winkler recommended to heat finely ground graphite with calcinated soda and sulphur in the covered crucibles as long as sulphur burns.After cooling, the sintered substance is boiled with water and then decanted. The residue is leached by diluted HCl which dissolves all iron present in this residue under evolving the gaseous H_2S. Finely dispersed graphite settles down after some time and small portions of quartz can be eventually removed by NaOH at high temperature.

An interesting chemical refinement of graphite was worked out by Luzi. According to him, graphite moistened by concentrated HNO_3 is heated. HNO_3 penetrates in the course of heating between the graphite molecules and causes its expansion. At the same time, particles of mineral impurities are releases as the distance of graphite molecules increases. Graphite prepared in this way is very plastic and suitable for pressing.

In 1899 Douglas brothers proposed, for example, refinement of graphite by means of HF. Nevertheless, the refining by NaOH and HCl essentially according to Schlaeffel method is mostly used in industrial practice.

1. Chemical Refining of Graphite in Industrial Practice

Decomposition of possible impurities caused by NaOH can be expressed by the following equations:

$SiO_2 + 2\ NaOH = Na_2SiO_3 + H_2O$

$Al_2O_3 + 2\ NaOH = 2\ Na/AlO_2/ + H_2O$

$P_2O_5 + 6\ NaOH = 2\ Na_3PO_4 + 3\ H_2O$

$TiO_2 + 2\ NaOH = Na_2TiO_3 + H_2O$

$V_2O_5 + 6\ NaOH = 2\ Na_3VO_4 + 3\ H_2O$

$Fe^{+3} + 3\ OH^- = Fe/OH/_3$

Acidic dissociation proceeds according to these equations:

$Fe^{+3} + 3\ HCl = FeCl_3 + 3\ H^+$

$MnO + 2\ HCl = MnCo_2 + H_2O$

$CaO + 2\ HCl = CaCl_2 + H_2O$

$MgO + 2\ HCl = MgCl_2 + H_2O$

If in addition HF is used in the leaching process, the following reactions can take place:

1. $SiO_2 + 4\ HF = SiF_4 + 2\ H_2O$
2. metal compound + HCl = metal chloride
3. metal compound + HCl = fluorchloride complex

On studying the reaction mechanism, scientists have come to the conclusion that the reactions proceed primarily according to eq. 1 and 2. All ash matters should be transferred into the solution, SiO_2 should evaporate as SiF_4. Alkaline reactions are accomplished by melting. After cooling the melt must be crushed and leached by water. Filtration of these alkaline products proceeds without great difficulties. After the additions of HCl, the voluminous gel of $SiO_2 \cdot n\ H_2O$ is formed as follows

$$Na_2SiO_3 + 2\ HCl + n\ H_2O = 2\ NaCl + H_2O + SiO_2 \cdot n\ H_2O$$

Many different compounds from the solution can be adsorbed on this gel and its filtration is not easy. Serious difficulties are also caused by melting with solid NaOH, carried out at higher temperatures (the optimum temperature is approximately at 320°C). In this way the product with maximum carbon content 96 - 98% wt. canbe manufactured.

Further method possibly suitable for the industrial application is so called alkaline calcination. It is based on the fact that the solubility of SiO_2 in NaOH is dependent on the crystal modification of SiO_2. Dissolving of quartz in the diluted NaOH proceeds slowly whereas tridymite is dissolved easily. In practice this method is carried out in the following way: Graphite raw material is heated up to 300 - 400°C, put into hot NaOH solution, boiled for some time and after filtration leached in HCl. This method has not been fully worked out yet in detail but the results reached in pilot plant tests show that at certain conditions the products having 99% wt. of carbon can be manufactured in such manner.

VI. APPLICATION OF GRAPHITE

1. Refractories

Due to its excellent refractoriness, thermal conductance and resistance to thermal shock, graphite is suitable for the manufacture of crucibles for reducing smelting. Crucibles from graphite were used in metallurgy already several hundreds years ago. The reducing property of graphite is also advantageous during melting of metals since it slows down the formation of oxides and slag. Graphite crucibles are made either with clay bond or with organic bonds. Organic bonds are used mostly in case of amorphous graphites. The products containing these microcrystalline graphites are frequently graphitized (see 1.3) after the normal ceramic fabrication. In this way, their quality can be substantially improved. To tell the truth, amorphous graphites are not suitable for the manufacture of crucibles. Pressing of such materials yields many problems (creation of microcracks, unsatisfactory resulting density). Moreover, they are not stable enough at high temperatures loosing mechanical strength and increasing porosity. Burning of amorphous graphites at higher temperatures takes place much more easier than that of flake graphite.

On the other hand, the coarse flake graphites are very attractive for the manufacture of crucibles. They are mixed with refractory clays which have good binding property and do not contain Fe_2O_3 and CaO. Magnesite is also frequently used in the bond here. The very important stage of the ceramic fabrication is pugging the humid body. Wetting of graphite flakes is very difficult because of its hydrophoby. Kneading machines used for this purpose must be really efficient.

After kneading, the body must mature for some weeks before forming. Careful drying takes place then at 60°C and firing continues at the temperatures of 900°C in the reducing atmosphere.

The softening of graphite crucible begins usually at 2000°C. The crucible of good quality should withstand 60 melts in average. There are also some technologies for the regeneration of graphite from worn-out crucibles.

Graphite can be used for mould dressing and similar purposes in metallurgical plants. The endurance of blast furnaces is sometimes improved when in the bottom of hearth the graphite bricks instead of fireclay bricks are applied. The layer between graphite bricks and metal hearth casing is also filled by graphite rammed lining.

2. Structure Ceramics

In the plants where explosives or explosive chemicals are manufactured, there is a danger consisting in the possibility of explosion due to the discharge of static electricity. In order to prevent from gathering of electric charges, floor tiles having necessary electric conductance are utilized for making the floors, pavements, etc. These special tiles are manufactured from graphite, clays and grog by means of ceramic fabrication processes. Firing must be carried out in saggars filled with coke powder to prevent tiles from oxidation. Graphite present in the body must form the interconnected matrix which enables the conductance of electric currents throughout the tile.

3. Electrical Engineering

Electrical conductance together with considerable chemical resistance make graphite attractive for the use in electrical engineering. For example, electrodes for different types of electric furnaces, heating elements for electric resistance furnaces, anodes for electrolyzers, bars for arc welding, electrodes for galvanic cells, carbon brushes for electric motors, etc. are made from graphite of high purity. Electrodes for arc furnaces and heating elements for electric resistance furnaces are also made from amorphous graphites. Very high purity must show graphites for the manufacture of electrodes used in spetrographs. For the steel-making arc furnaces, electrodes with diameter in the range 130 - 500 mm are manufactured. Their specific consumption is in about 9 kg of graphite per 1 ton of steel.

4. Lubricants

Graphite represents the important part of many lubricants used in nearly all branches of the industry. Its molecular structure determines softness, greasy feel, high abradability. Lubricants must form thin viscous film between the friction planes.

Viscosity of liquid lubricants decreases with rising temperature. Due to this fact, the loading of friction parts should have to be substantially decreased at higher temperatures, It is advantageous in this respect to utilize lubricants with the solid phase content (e.g. graphite or MoS_2). For this purpose chemically refined colloidal graphite is usually applied.

Colloidal very finely ground graphite penetrates during run into the surface pores of lubricated part, forming smooth resistant film. This film cannot be easily torn off and moreover it conducts away the heat which contributes to the better cooling of e.g. lubricated bearing. Graphite lubricants are mostly either mixtures of pure flake graphite with grease or oil suspensions of colloidal graphite or water suspension of colloidal graphite.

5. Manufacture of Pencils

Modern way of the manufacture of pencils has its origin in the discoveries by Hardmuth and Conté in 1790. Since that time black leads have been produced from the mixture of graphites and washed clays. Wet grinding of these components is carried out in so called czech mills. Ratio graphite/clay determines the hardness of pencil. Finely ground mixture must be dewatered, dried, kneaded and carefully homogenized. Then it comes forming, drying of compacts and in the end firing in a reducing atmosphere.

6. Nuclear Physics

Graphite serves in the nuclear reactors as moderator, reflector or shielding layer. It retards and reflects neutrons in the reactor and protects the environment against the effect of radiation. During emission of neutrons from U 235, U233 or Pu 239 nuclei, these particles are scattered in all directions. Graphite is suitable for the retardation and reflection of neutrons because of its molecular structure. The retardation effect is important not only with respect to radiation but also for the smooth course of the fission chain reaction. During fission of U 235 nuclei certain neutrons move with substantially greater velocity than "ordinary" ones. These "fast neutrons" cannot be used for the fission purposes. Graphite retards them so that their velocity is decreased to the degree which is approximately equal to the velocity of thermal motion of the molecules. The fission chain reaction can be thus controlled in this manner. Otherwise this reaction would proceed with extraordinary rapidity and the explosion as in the atomic bomb would occur in a short time.

As a moderator graphite is of course not as good as heavy water but the substantially lower production costs eliminate this disadvantage. Graphite construction elements for the nuclear reactors must show nearly 100 % purity and it is necessary to manufacture them with extraordinary precision. Forming of these products takes place at the pressures of 300 MPa. Especially the presence of boron, calcium, titanium, vanadium and elements of rare earths is harmful.

Radioactive radiation supports the growth of graphite crystals /Wigner`s effect/, which might be dangerous for the run of the nuclear reactor in the whole. For this reason, all graphite parts of the reactor must be constantly supervised.

Beside this, graphite has found application in many other industrial sectors as for example in colouring of glass, in special coatings, pigments, fillers, etc.

VII. FINAL NOTE

It can be said that there is renewed interest in graphite in our times. It is especially due to its application in nuclear techniques and as an excellent refractory material that graphite has gained world wide attractiveness. It is true that many products can be made from artificial forms of graphite but natural flake graphite has still maintained its important position among the family of graphite raw materials. Only coarse flakes lend the graphite good moulding property and outstanding thermal endurance.

Moreover, graphitization of amorphous graphites is a very expensive process. Many of the old deposits have been gradually exhausted. The classical sources of natural graphite in Austria, German Federal Republic, Mexico, Madagascar, Ceylon, Norway, USSR, China will not be probably capable to satisfy the growing demand in the near future. For this reason the search for new deposits of natural graphite should be one of primary economic interests of each country.

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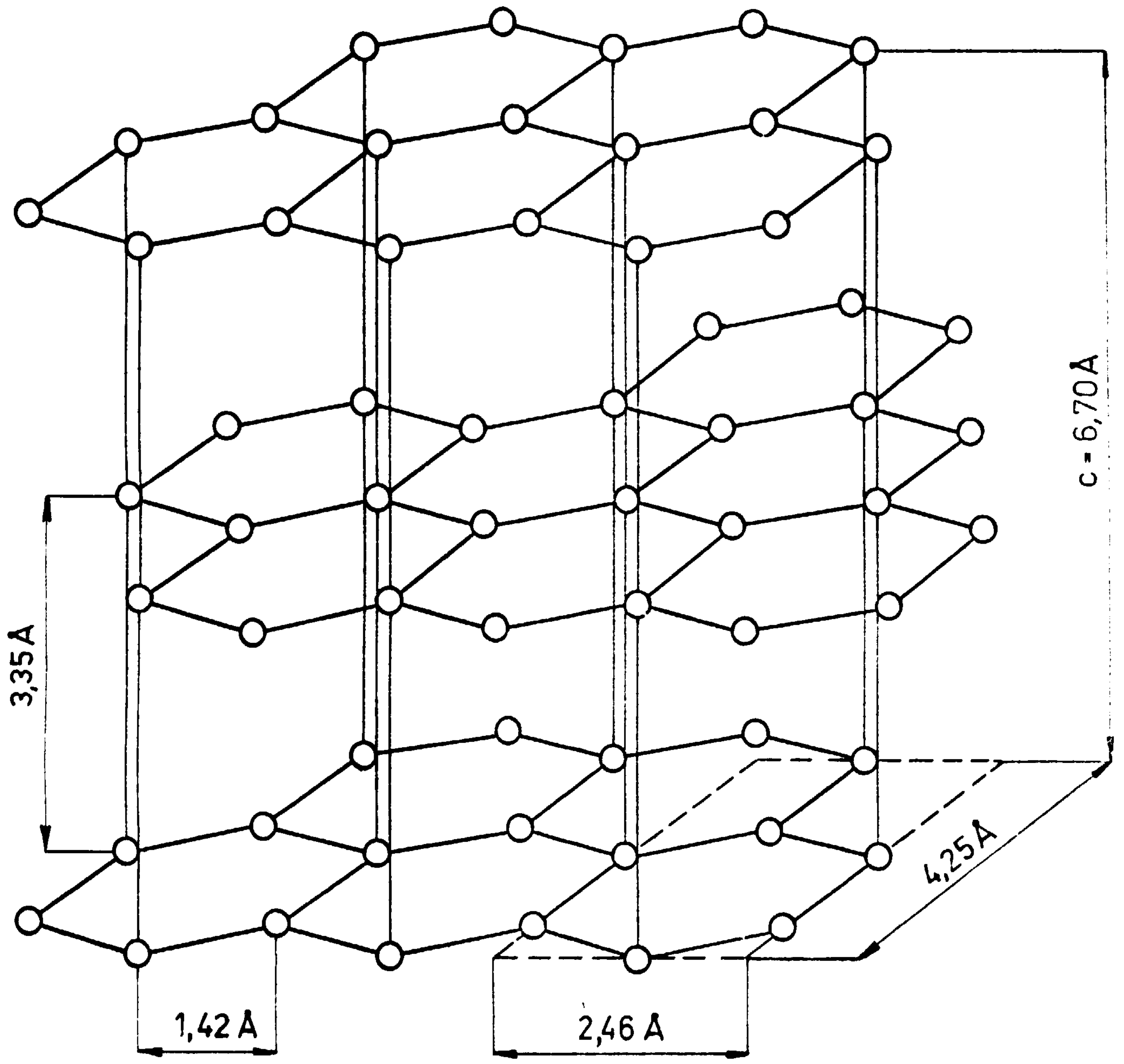

Figure 1: Crystal lattice of graphite

/Ref. 3/

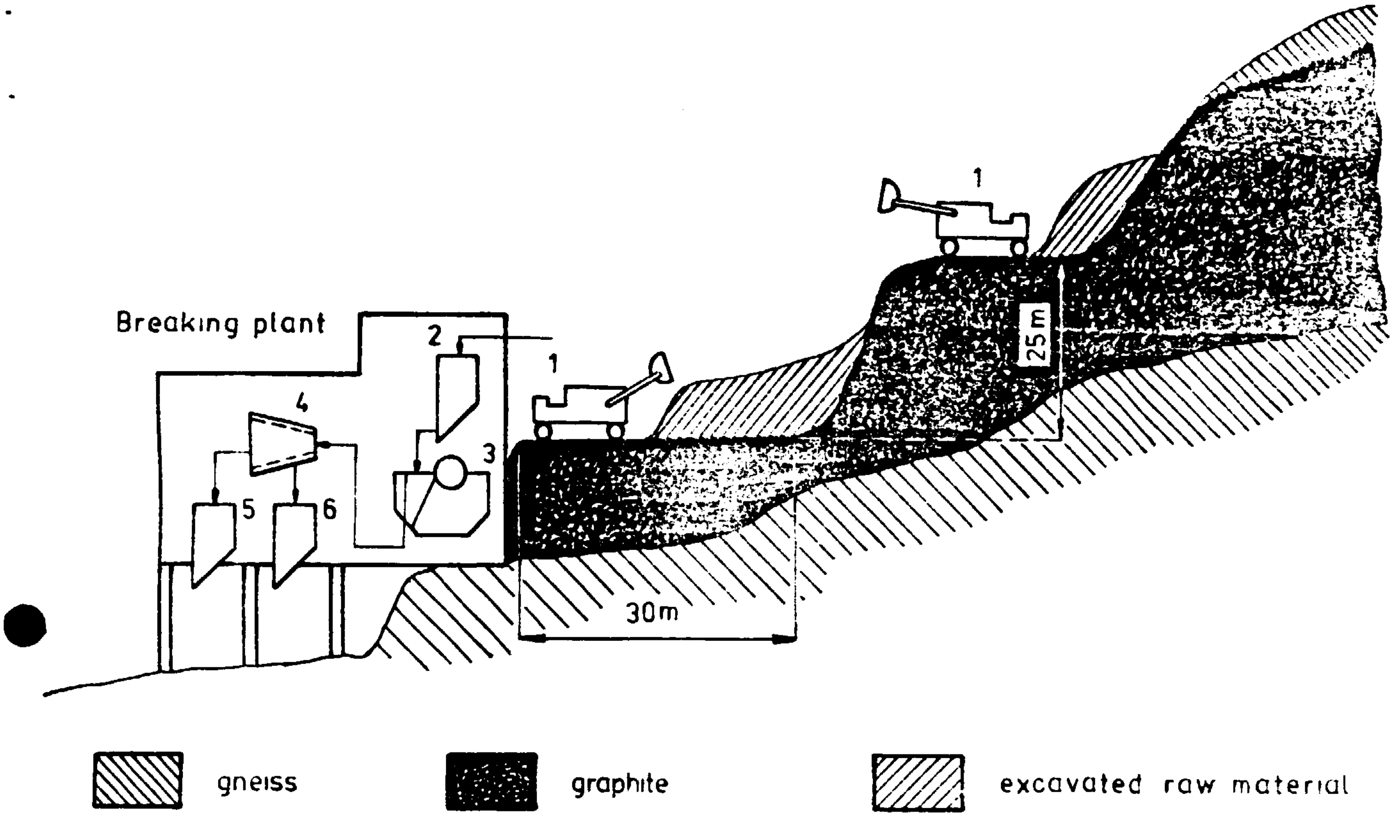

Figure 2: Cross section of the deposit at Zettlitz (Austria) /Ref. 3/

1 = excavator; 2 = silo; 3 = jaw crusher; 4 = trommel /meshes 100 mm/; 5, 6 = crushed graphite stone

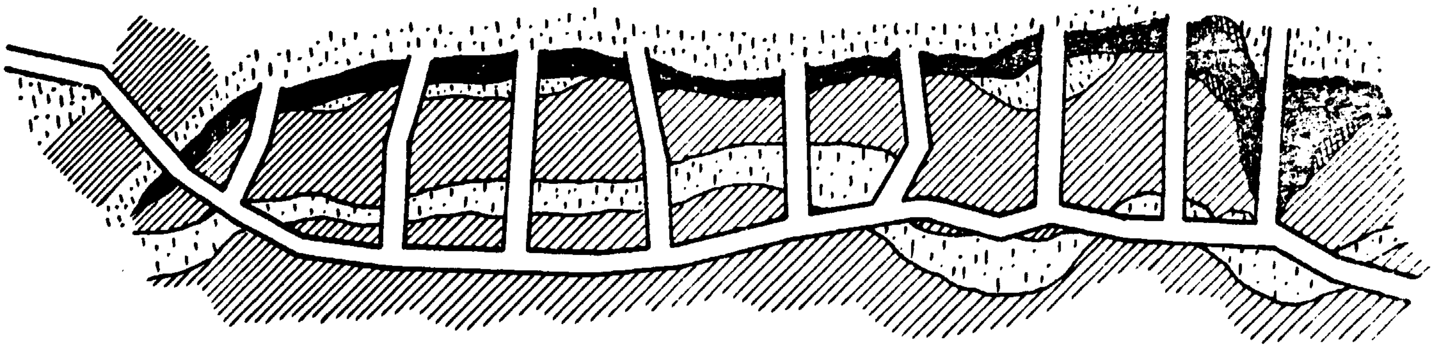

Figure 3: Underground mine Alois at Malé Vrbno (Czechoslovakia) /Ref. 3/

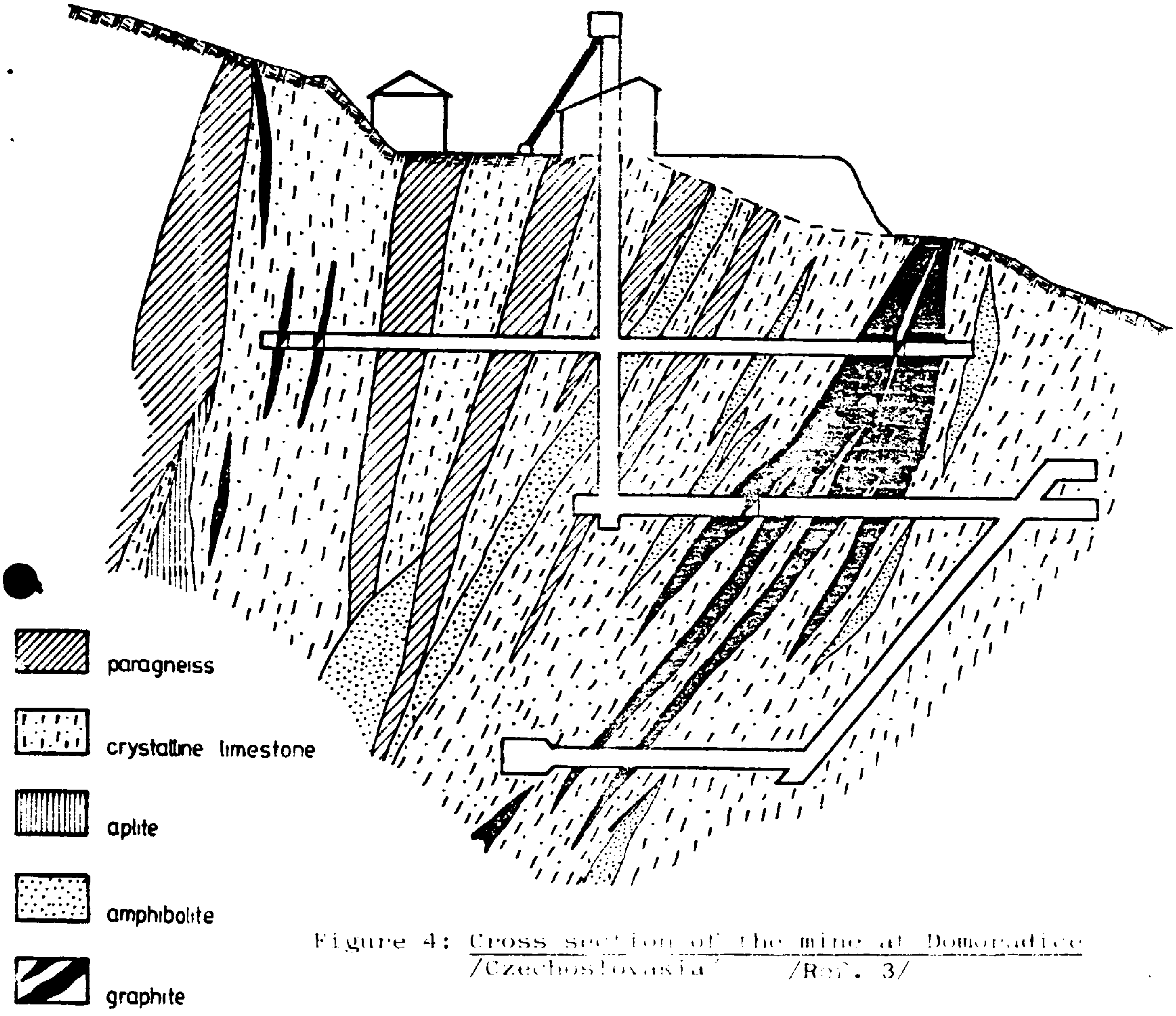

Figure 4: Cross section of the mine at Domoradice /Czechoslovakia/ /Ref. 3/

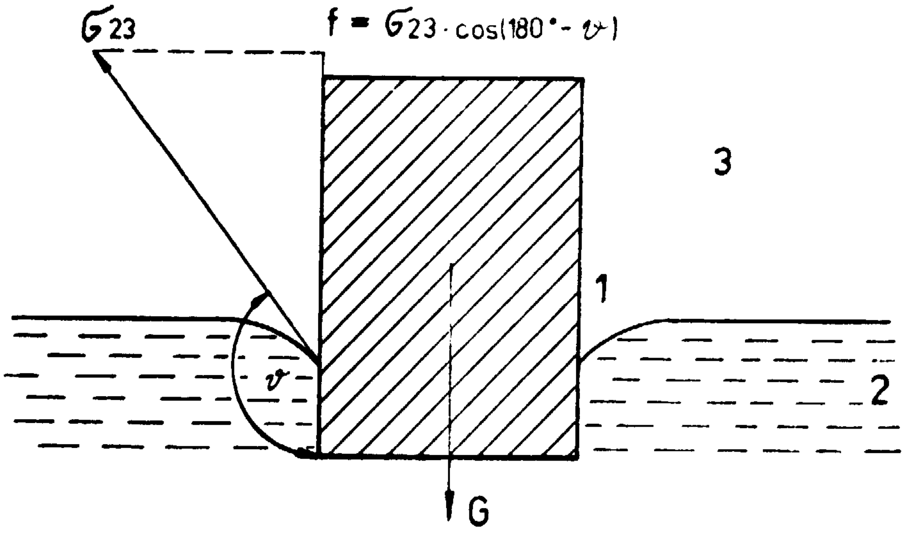

Figure 5: Graphite grain on the surface /Ref. 3/

1 = solid phase; 2 = liquid phase; 3 = gaseous phase; ϑ = contact angle
σ_{23} = surface tension between gaseous and liquid phases

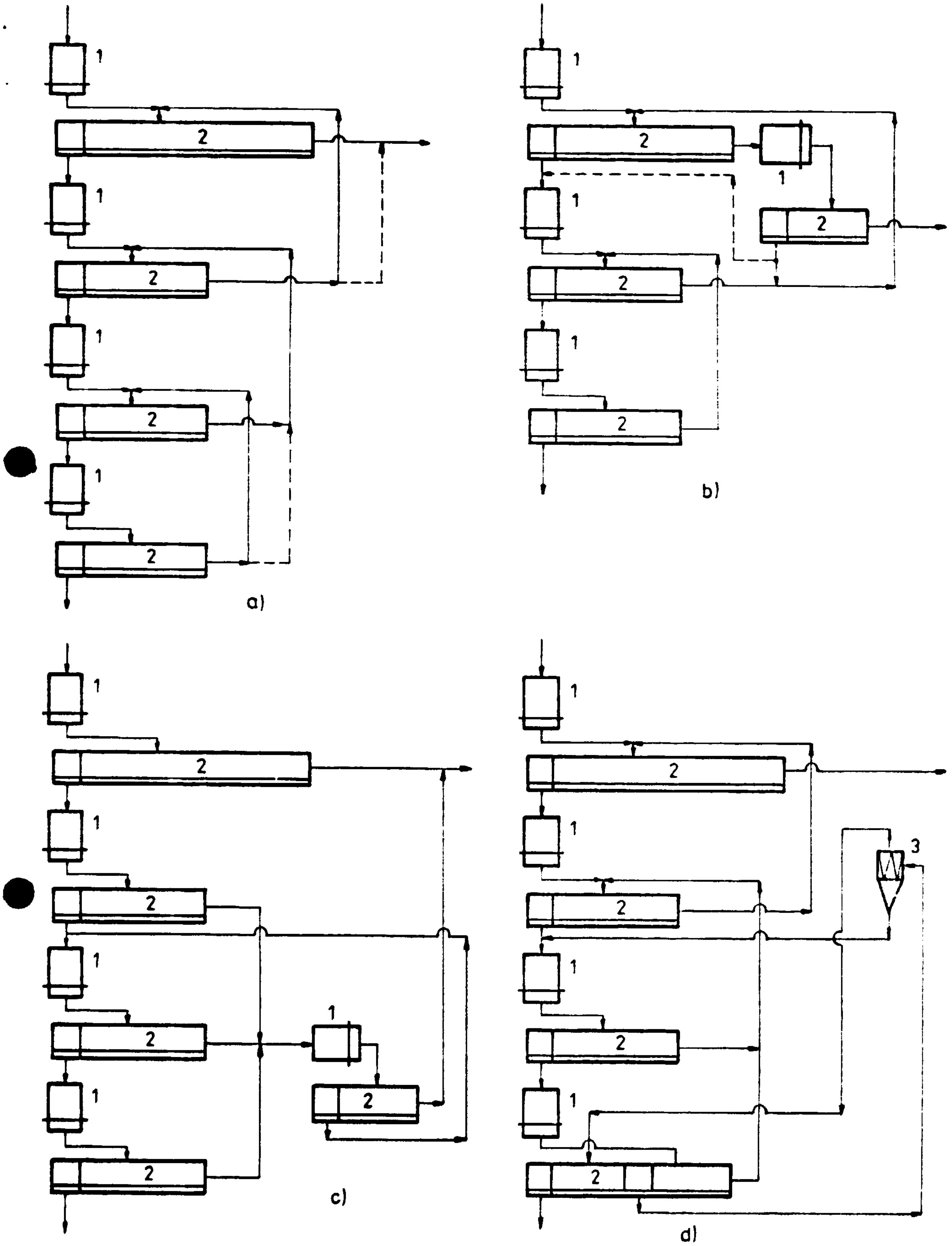

Figure 6: Schemes of basic systems of graphite flotation /Ref. 3/

1 = ball mills; 2 = flotation cells;

3 = hydrocyclone