APPLICATION OF NEW LIGNIN GROUTS IN SEALING OF SOILS

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ABSTRACT

The paper includes four parts t.e. studies on aluminiferrous chromium lignin, experiments on pollution range in grouting with chromium lignin, studies on low toxic lignin /expecially chrome slag lignin/ and studies on non-toxic lignin /sulfate lignin/. A brief account is given on the significance of using new lignin grouts as a chemical grout material from the viewpoint of utilizing industrial waste, enlarging the sourse of grout material, decreasing cost and limiting environmental pollution. Main results of laboratory experiments are given in the article including properties and formulation of new lignin grouts, factors affecting setting time and strength of congelation, the permeability and viscosity as well as toxicity of new lignin grouts. All these provides the experimental basis of the application of new lignin grouts in engineering practice. Practical examples of waterproof sealing of inclined shaft stations, signal chambers, pourer substation chambers and dam's foundations are described in the last part of the article. 95 % waterproof efficiency is achieved. In conclusion, the author highlights the advantages and prospects of the use of chrome slag lignin and peroxy /mono/ sulfate lignin in the field of waterproof sealing. The author also points out the direction for further research on chrome slag lignin and peroxy /mono/ sulfate lignin.

INTRODUCTION

With the developments of mine constructions and other underground engineerings, geology conditions to be met with become more and more complicated. It is difficult to meet all the needs of engineering sealing with suspended solution class grouts such as cement or the like. Since the middle term of 60'ty years, chemical grouts, like sodium silicate formulations, lignosulfites, phenoplasts, acrylamides, polyurethane and so on, have been applying in many mine underground engineerings such as chambers ore stores, shafts, drafts, civil underground building, water dam foundations and so on. In most of chemical grouts, there exist the problems that the expense is cost, that the strength is lower and that the environment is polluted. The grouts testing group of Northeast Institute of Technology has made laboratory test and field investigation in the changing nature research of chromium lignin class grouts for near ten years and achieved good technological and economical results.

I. STUDIES ON ALUMINIFERROUS CHROMIUM LIGNIN

Generally, chromium lignin is ferrous chromium lignin whose compressive strength of sand consolidation os lower, about 5 kg/cm². That the strength in fixing middle-coarse sand in the building shaft with chromium lignin reached over 10 kg/cm² was required on a certain Iron Mine in Henan Province. The grouting testing group of N.E. Institute of Technology has proceeded the basic formultation tests of six promoters: $AlCl_3$, $Al_2/SO_4/_3$, $CuCl_2$, $CuSO_4$, $FeCl_3$ and H_3PO_4 and selected a better formulation to make consolidation tests of quiet water and moving water in the device of consolidation test. /Fig. 1./. In the tests, the formulation whose compressive strength was high to 24 kg/cm² was obtained /Tab.1/.

Promoters have very great influence on the strength. The effects of aluminic salt are better than that of other salts but when amount of aluminic salt added is beyond the given value, the strength lowers on the contrary /Fig. 2./. Under the condition of the same amount of metal salt, to add chloride is better than that sulfate.

The pourable distance of aluminiferrous chromium lignin in fine, middle and coarse sand is measured to be 0.75-1.50 M by using the device for measuring pourability of grout material /Fig. 3./. In the field grouting investigation in Batai Iron Mine, Henan Province, in 1973, an aluminiferrous chromium lignin curtain 2.8 M /long/, 1.3 M /high/ and 0.5-0.6 M /thick/ was got /Fig. 4./. In 1981, Mine in Xijing, aluminiferrous chromium lignin has been employed in a surface pregrouting test, whose formultation is the following: sulfate waste liquor 26 % /17.5 Be/ 50 ml; sodium bichromate 10 g, sulfate of alumim 1 g, cupric sulphate 0.4 g, ferric chloride 0,4 g. Water add to 100 ml. The viscosity was 3 c.p. and the pourability was good.

II. EXPERIMENTS ON POLLUTION RANGE OF GROUTING

$Na_2Cr_2O_7$ in chromium lignin is a violent toxic medicine and therefore, in grouting on stratums, there may be the problem of underground water being polluted by Cr^{+6}. With a view to solve the problem, MEIT has experimented and measured on the pollution range of chromium lignin grout, which has rovided the bases for using it.

1. Immersion Experiment

The solidifying sand body that had been made as the formulation B in Tab. 1a was immersed in water and its draw-off rate relatives to the immersion time and $Na_2Cr_2O_7$ content in the formulation.

2. Adsorption Experiment

A steel cylinder has been taken and the sand has been filled in it. The immersion fluid has filled in and been filtered time and again, and then based on the chemical examination results the saturated adsorption quantity of the sand on a unit volume to Cr^{+6} has been calculated. The test results are shown in Tab. 2. The test proved that sand has some absorbing action to Cr^{+6}. The finer the sand, the greater the saturate quantity absorbed by per leter sand.

3. Field Investigation and Results on Pollution Range

In order to grasp further influences on pollution degree, the experiment of measuring the pollution on-the-spot has been again made in Batai Iron Mine. The results of the experiment are shown in Tab. 3. The following conclusions are drawn from the tests:

1. Under the same conditions, draw-off rates of Cr^{+6} are concerned by immersion times. If immersion in fine sand three days, the draw-off rate is 3.8 %, and ten days, 13.2%.

2. Owing to the plysic action of sand, Cf^{+6} immersed in water produce the phenomenin of adsorption to sand in the cause of it being saturated. From the experiment to know, saturate quantity absorbed by per liter sand is related to the size of sand grain /surface area/. /Tab. 3/.

3. According to the results of practical measuring to the grouting sand stratum deep from 21.2 to 27.5 M. the greater the grouted quantity, the larger the pollution range /Tab. 3/. Moreover, Cr^{+6} craated by grouting with chromium lignin will be reduced gradually as time elapses.

During the past ten years, NEIT has been studying chromium lignin on two sides as follows:
/1/. to reduce the quantity of the chromium salt in the formulation of chromium lignin grouts;
/2/. to use other chemicals to replace chromium salt.

III. STUDIES ON LOW TOXIC CHROMIUM LIGNIN

/I/. Chlorizate Chromium Lignin

Japanese scholars Tianzhong, Bantian and Qianshon thought that gelatinate reactive hypothesis of lignin was caused by oxidation bridge linkage of phenol nuclous. /Fig. 5/. Therefore, lignin also causes the gelatinate reaction with peroxy /mono/ sulfate, potassium ferric oxalate and so on. On this basis, MEIT has compared many oxidizers and finally, bleaching powder has been selected, which may replace a part of $Na_2Cr_2O_7$. Its formulation is listed in Tab. 4.

The following conclusion from laboratory tests have been got:

1. Since chlorizate chromium lignin is used and a part of $Na_2Cr_2O_7$ is replaced by filtrate of bleaching powder, the amount used of $Na_2Cr_2O_7$ is decreased by 56 % and the draw-off rate is decreased by 28 % that of aluminiferrous chromium lignin, so that the pollution of the underground water has been decreased and it may improve on the waste solution and has the disinfecting action. The results of immersion experiment of two formulations are listed in Tab.5.

2. A part of $Na_2Cr_2O_7$ is replaced by bleaching powder whose source is extensive and cost is expensive, so that the cost is decreased by one third. Since it is complicated that bleaching powder is produced and fillered in a large scale of grouting engineerings, the semi-industrial experiment has not been made.

/II/ Chrome Slag Lignin

Chrome slag lignin whose main agent, curing agent and promoter all may be made and be prepaired by the waste products is a kind of typical grout materials utilized the waste products. It not only has low price and wide sources, but also lowers toxicities of grout and reduces pollutions of circumstances, which has better economic effects in the industrial experiments.

1. Formulation /Tab. 6/

The curing agent is chrome slag with PH=8.8, whose aluminate content is 29-31 %, chromic salt 15-25 %, calcic salt 3-5 %, magnesum salt 2.7 %, iron salt 0.15-3.7 % and other refuses. After acidizing, $Al/OH/_3$ in the slag have changed into $AlCl_3$ and chromate have changed into bichromate and become liquid purified of acidific chrome slag.

/1/ Setting time
The decisive factors to have influence on setting time are: quantity of $FeCl_3$ used and temperature of reaction. According to the formulation in Tab. 6, the real line in Fig. 6 has been obtained. The more quantity of $FeCl_3$ used, the shorter setting time. In Fig. 6, the detted line shows influence of temperature on setting time. The higher temperature, the shorter setting time.

/2/ Compressive strength
The compressive strength of chrome slag lignin enlarges as lignosultin, chrome slag and as shown in Fig. 6. Adding to a certain quantity of borax may enlarge the strength.

/3/ Permeability
Used N-55 OSMPSCOP and under water head 640 cm, chrome slag lignin has been measured not to be seepage for 7 hrs.

/4/ Viscosity
It is similar to that of chromium lignin. Change circumstances of viscosity of chrome slag lignin in the course of gelling are shown in Fig. 8.

2. Field investigation

The chrome slag lignin was first applied to stop up seepage at the incline shaft station, signal chamber and power substation chamber in Xangdong Iron Mine. The station and signal chamber had crack water and the speed of seepage water was 2300 ml/min. The crack width in the power substation chamber was tiny and the speed of seepage was larger many times than that of the station on the raining season. Due to cement is difficult to meet the needs of grouting, the plan that grouting with chrome slag lignin would be emploied had been decided. The grouting time of two chambers was about one week and the cost prices of grouting were 67.7 Yuans per meter of the draft. /Fig. 9, 10/.

The speed of seepage water was 115 ml/s after grouting and the rate of blocking water was 85 % in the signal chamber. The seepage water have been also stopped at the power substation chamber. After a year, the effect observed had not changed in spite of on the raining season.

The result showed: it can be carried on that chrome slag lignin is made use of to replace $Na_2Cr_2O_7$. It has better pourability and the toxicity of grout is lower. Its main functions are similar to ordinary chromium lignins. The production cost of slag lignin was lower 50 % than that of chromium lignin, which the cost of one m^3 grout required about 200 Yuans. In the present, this is the cheapest one of grouts in chemical grouting.

IV. STUDIES ON PEROXY /MONO/ SULFATE LIGNIN NON-TOXIC LIGNIN

Above mentioned formulation of lignin needs also a certain amount of chromic salt and the toxicity was not destroied. Starting with study of reaction hypothesis of sulfate lignin to oxidizer and through many tests, NEIT has made up the non-toxic lignin grout /not to contain $Na_2Cr_2O_7$/-- peroxy /mono/ sulfate lignin. The formulation of peroxy /mono/ sulfate lignin is shown in Tab. 8.

1. The setting time result of the test /at RT 15°C/ is shown in Fig. 10. It is known from Fig. 10 under 40 % that the higher the solid contained in lignosultin, the shorter the setting time. When weight of $/NH_4/_2S_2O_7$ used exists about 5-5.5 g, the setting time become the shortest and density of gelation become better. But under 3 g of $/NH_4/_2S_2O_7$ used, the gelatin is too soften to shape. And without adding $/NH_4/_2S_2O_7$ the grout appears alkalinity /PH=10/ reaction, while acidic grout can't solidify under circumstances of alkalinity. On ground of this formulation the test has showed that the lowest amount added to make peroxy /mono/ sulfate into $/NH_4/_2S_2O_7$ solidified must be over 30 % of the dry powder content in lignosultin, while over 50 % to the gelatin resistance water. The more amount of $CuCl_2$ used, the shorter the setting time and better the density. Without added $CuCl_2$, the temperature of reaction of grout is low and grout does not gelatinate for a long time, which it is better to add 1-2 %. To change temperature has also great influence on the setting time, which the result is similar to other chemical grouts.

2. The compressive strength
The test results surreied have shown that average strength reaches about 5 kg/cm² so that the demands for blocking up seepage could be met.

3. The viscosity of peroxy /mono/ sulfate lignin has been measured to be 4 cp.

From the above mentioned tests known:

/1/ Because the peroxy /mono/ sulfate lignin do not require completely chromic salt as curing agent, it is non-toxic so that the pollution to underground water sources is exterminated and the new pathes for grout materials of lignin kind to be obtained in our country are opened.

/2/ The tests prove that the gelatin of peroxy /mono/ sulfate lignin does not dissolve in water, dilute acidic liquid and dilute alkalinity liquid, so that whose chemical properties are steady. The gelatins of peroxy /mono/ sulfate lignin immersed in water, dilute acid liquid and dilute alkalimity liquid take place to expand so that is advantage to block seepages.

At the water dam in Jinduicheng Molybdenum Mine, Shanxi Province, there are tiny cracks in the dam's foundation. Experiments had proved that cement pouring did not meet the need, so that chemical grouting has been emploied.

In 1979, emploied grouting with peroxy /mono/ sulfate lignin, NEIT has completed the semi-industrial experiment of dam's foundation grouted curtain within the dam corridor and have achieved better effects of grouting /Fig. 12/ /Tab. 9/.

SUMMARY

1. The aluminiferrous chromium lignin particularly the promoter being of $AlCl_3$, can greatly increase the strength /about 20 kg/cm/ and improve on the pourability /3 cp./

2. The main, curing agents and promoter used in chrome slag lignin can be made from the waste products and its grout cost was reduced by 50 %, compared with that of sodium bichromate. It is the one of the cheapest chemical grout materials in the present.

3. On the basis of low toxic lignin, NEIT has used $/NH_4/_2S_2O_7$ as curing agent to replace all chromic salts and has made out sulfur lignin that is peroxy /mono/ sulfate lignin so that has eliminated the pollution to underground water sourse and opened up a new path for the grout materials of lignin. In mine semi-industrial experiments, better technology and economy targets have been achieved in grouting with chrome slag lignin and peroxy /mono/ sulfate lignin.

4. Author points out that further researches will be made in the direction of strength and lastness on chrome slag lignin and peroxy /mono/ sulfate lignin.

References

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2 Experiments on contaminating influence in grouting with chrom.lignin . NEIT et al. "Mining Technology" No.1. /1977/
3 Studies on formulation of low toxic chromium lignin. Du Jiahong et al. "Nonferrous Metals" No. 5. /1977/
4 Studies on formulation of peroxy /mono/ sulfate lignin. Du Jiahong et al. "Nonferrous Metals" No. 3. /1978/
5 Studies on chrome slag lignin and its application. Du Jiahong et al. "Nonferrous Metals" no. 2. /1980/

List of Tables:

Table 1.
Changing nature studies on chromium lignin

Topic	Problem	Test	
		Date	Place
Studies on alu-miniferrous chromium lignin	Increasing compressive strength	1973	Batai Iron Mine Henan Province
	Improving pourability	1981	Mine in Xijang
Experiments on pollution range in grouting with chromium lignin	Measuring pollution range	1974-1976	Batai Iron Mine Henan Province
Studies on low toxic lignin	Lowering Cr^{+6} content	1977	Like above
	Utilizing waster	1980	Xiangdong Iron Mine, Hunan Province
Studies on non-toxic lignin	Exterminating pollution	1978	Gingdui Cheng Molybdenum Mine Shanxi Province
		1981	Daiyao Copper Mine Yunnan Province

Table 1.a

Physical nature of aluminiferrous chromium lignin

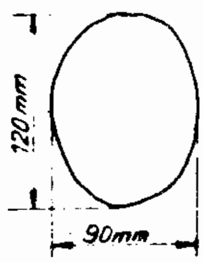
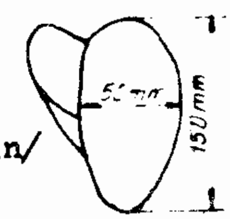
	A	B
Formulations	sulfate waste liquor /45%/ 100ml, $AlCl_3$ 20g, $Na_2Cr_2O_7$ 15-20 g, H_2O add to 200 ml.	sulfate waste liquor /45%/100 ml, $Al_2/SO_4/_3$ 20 g, $CuSO_4$ 2 g. H_2O add to 200 ml.
S.C. /g/cm³/	1.17	1.20
Viscosity/C.P./	2.6	3.6
Setting time/min./	6	7
Comp. strength /kg/cm/	17-24	17-24
Test in device /Fig. 1./ /in moving water/ outlook /velocity/	 very good /25 ml/min/	good /29 ml/min/ 

Table 2.

Sand standards	Coarse 0.63-2mm	Moderate 0.31-0.63mm	Fine 0.12-0.31 mm
quantity /l/	17.44	17.44	4.00
absorption time /days/	13	13	10
absorption /fitter/ numbers	39	39	50
quantity of absorpt.sol/ml/	3100	3280	4100
chromium in the absorpt. sol /mg/l/	27.32	27.32	61.52
saturate q. abserbed per l. sand	4.82	5.12	40.72

Table 3.

Relation of the grouted quantity of chromium lignin to pollution range

Date	Chromium lignin grouted quantity /M/	Chromium lignin $Na_2Cr_2O_7$ content /ton/	Pollution radius /M/	Non-pollution radius /M/
1976. 7-11	5.51	0.41	3.5	7.0
1976. 7-11	7.35	0.55	5.0	8.5
1975. 7-9	102	7.65	12.0	20.0

Table 4.

Comparison table of chromium salt content and cost of chlorizate chromium lignin with chromium lignin /Al/

name of grout	raw material	formulation	explanation
chlorizate chromium lignin /C/	Ls /40%/ $Na_2Cr_2O_7$ $FeCl_3$ Bleach powder /1g/ml/ borax H_2O	100 ml 6.6 g 13 g 34 ml 8 g 50 ml	1. 1m grout requires 207 Yuan. 2. When RT is 23-28°C, setting time is 8'-29'.
Aluminiferrous chromium lignin	Ls 40 % $Na_2Cr_2O_7$ $Al_2/SO_4/_3$ $CuSO_4$ H_2O	100 ml 15 g 20 g 2 g 63 ml	1. 1 m grout requires 305 Yuan. 2. When RT is 23-28°C, setting time is 6'-15'.

Table 5.

Comparison of results of immersion experiment of chlorizate chromium lignin with aluminiferrous chromium lignin

Formulations	immersion time/days/	immersion water/1/	Cr^{+6} content in sol./mg/1/	comparing of Cr^{+6} immersed out
Chlorizate chrom.lignin /C/	7	4	19.93	72 %
Aluminiferrous chrom. lignin /B/	7	4	27.32	100 %

Table 6.

Comparison table of the formulation of chrome slag lignin with chromium lignin

Formulation	chrome slag lignin		chromium lignin F
	D	E	
Raw material and proportion/100/	Ls/33%/ 50ml slag liq.-/1/25ml $FeCl_3$/50%/10-20ml H_2O add to 100ml	Ls/40%/ 50ml slag liq.-/2/30-50ml $FeCl_3$ /50%/10-20ml H_2O add to 100 ml.	Ls/40%/50ml $Na_2Cr_2O_7$ 8g $FeCl_3$/50%/10ml H_2O add to 100ml
Properties	1.RT 14 C, setting time 2'-40' 2.strength 6.5 kg/cm² 3. viscosity 45s	1.RT 8.5 C, S.t. 1'-150' 2.strength 8.8 kg/cm² 3.viscosity 47s	1.RT 20C, s.t. 1'-30' 2.strength 8 kg/cm² 3.v - 27s

Note: slag liq. - /1/: liquid contains 1g slag; S.C. 1.22.
slag liq. - /2/: acid-treated liquid, appearance presents orange-red, S.C. 1.22, PH 6.2.

Table 7.
Survey of Cr^{+6} content

formulation	gelatin /cm/	immersion time /Day/	immersion water /ml/	Cr^{+6} content /ml/l/	comparing of draw-off rate /%/
D/Tab.6./	48	28	200	6.5	30
F[x]	48	28	200	22	100

[x] Ls/30%/ 50ml, $Na_2Cr_2O_7$ 8g, $FeSO_4$ 2g, borax 3g, H_2O add to 100ml.

Used the draw-off rate of Cr^{+6} to calculate, the toxicity of slag lignin is lower 70 % than that of ordinary lignin.

Table 8.

Raw materials		color & shape	formulations		
			G	H	I
main agent	lignosultin 40%	black sticky	50ml	50ml	70ml
curing agent	$/NH_4/_2S_2O_7$	white solid	10-11g	7g	8g
promoter	$ZnCl_2$	white solid	-	2g	2g
	NH_4Cl	white crystal	3.2g	3.2g	-
	$CuCl_2$	green crystal	0.4g	0.4g	0.1g
	$FeCl_3$	brown solid	1-2g	-	-
	NH_4OH/NH_3 25%/	colorless liq.	4ml	4ml	-
	p-1	white solid	-	-	4.5g

Table 9.

The grouting effects at the foundation of water dam in Jindui Cheng Molybden Mine

Proce-dure	Hole num-bers	Sec-tion num-bers	W value of pressuring water /1/min.M.M./						Ave-rage ω 1/minMM	Com-pare
			0.0001		0.0001-0.001		0.001-0.01			
			S.N.	%	S.N.	%	S.N.	%		
before grou-ting	3	7	-	-	3	42.8	4	57.2	0.00101	after grou-ting than before gr. W lower 76.2%
after grou-ting	3	5	2	40	3	60	-	-	0.00024	

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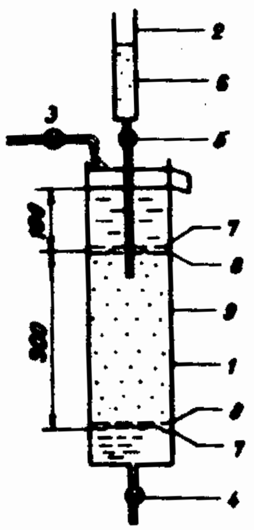

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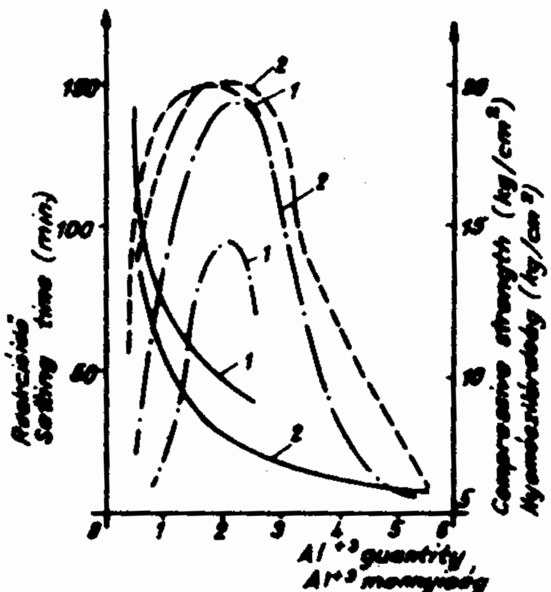

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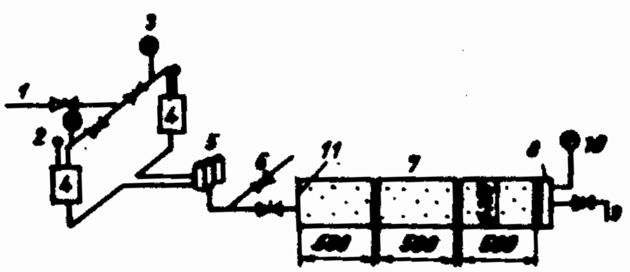

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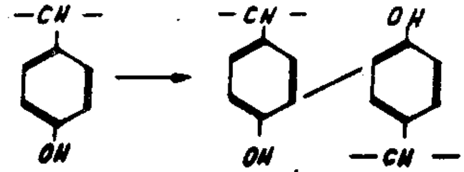

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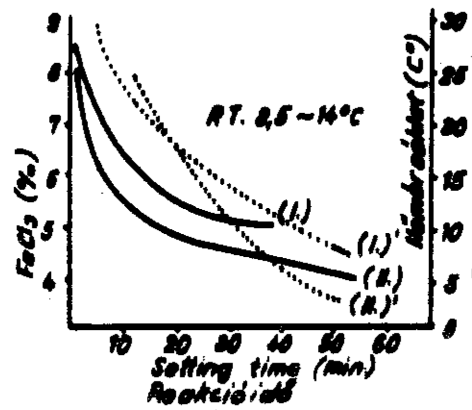

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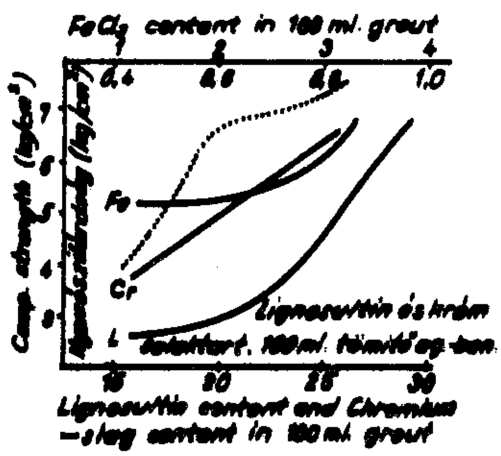

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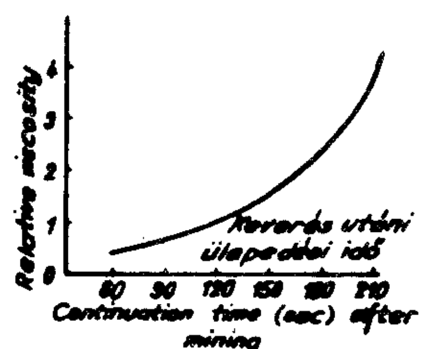

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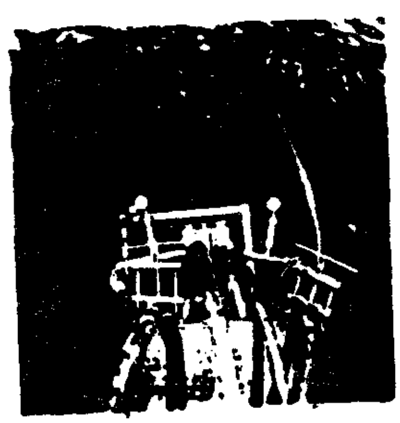

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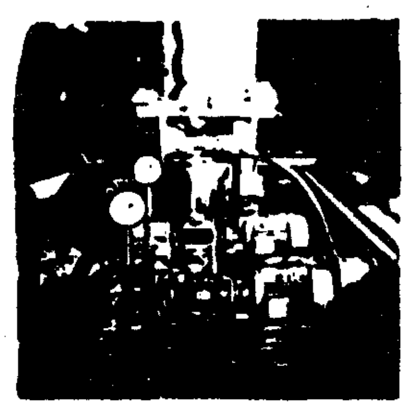

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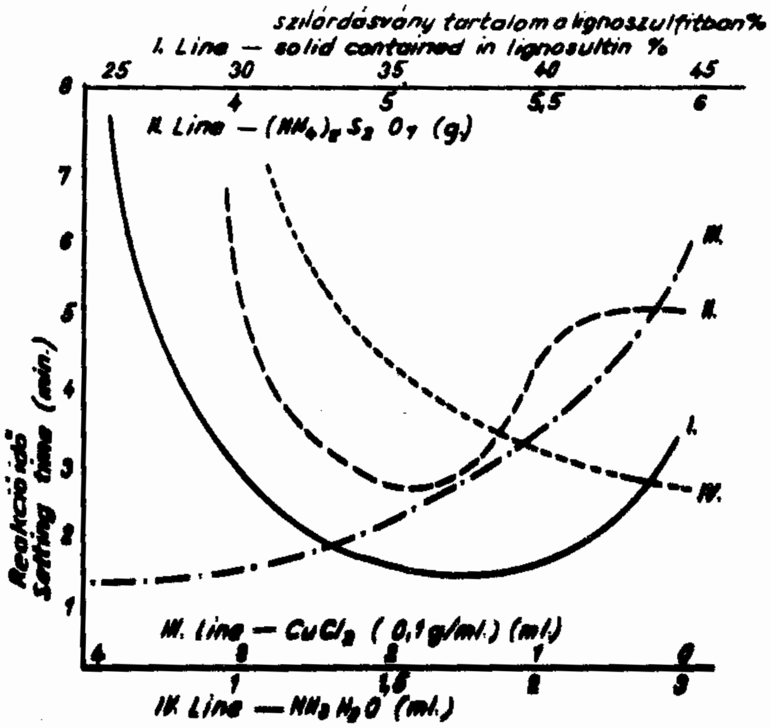

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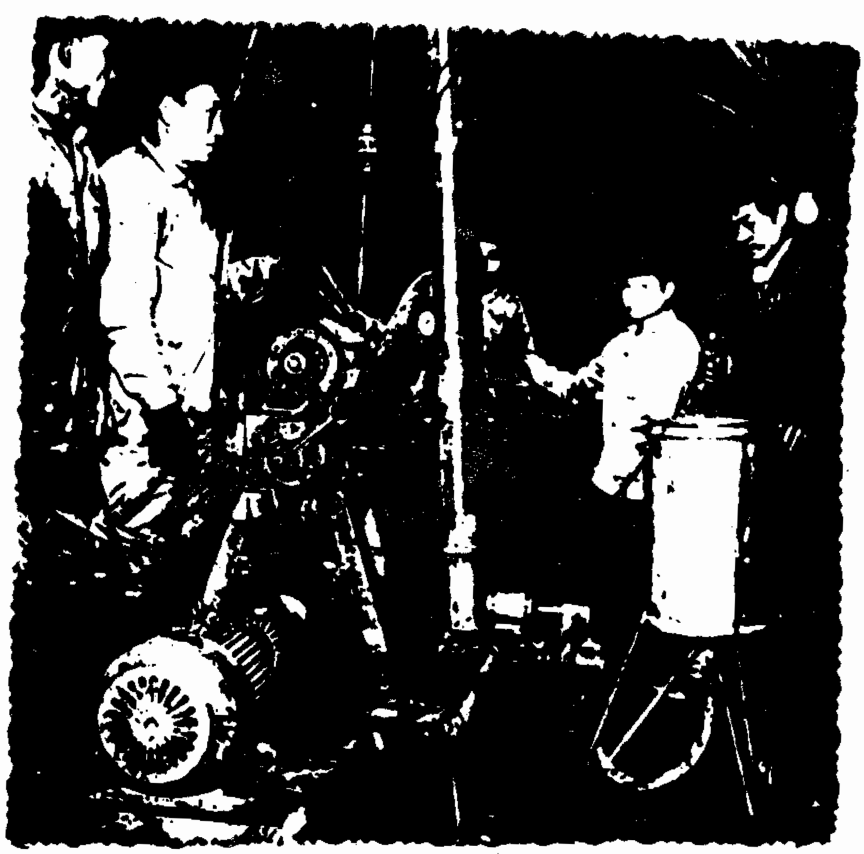

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