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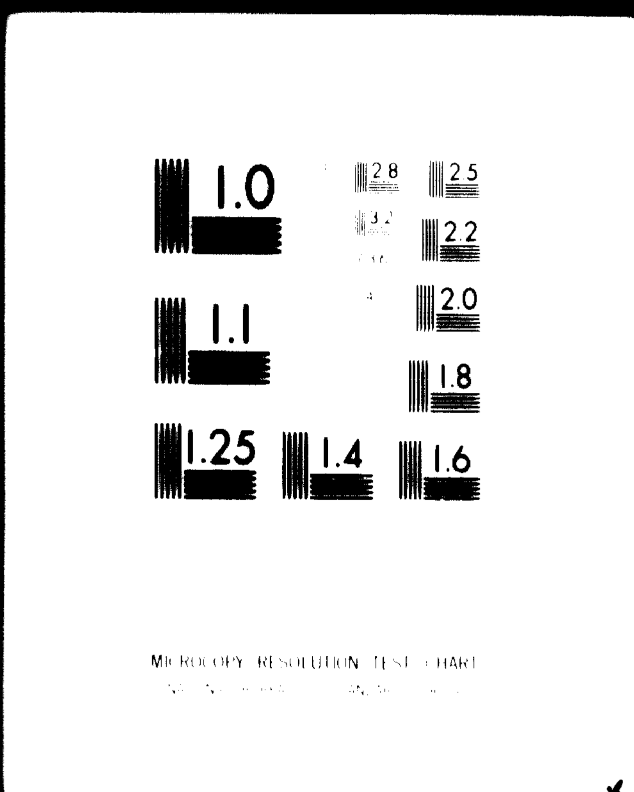

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TECHNOLOGICAL TESTING OF ILMENITE CONCENTRATES

/laboratory investigations/

Carried out by the All-Union Research and Design

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ABSTRACT

The report features the results of laboratory investigations concerning the technological testing of the indian ilmenite concentrates. There have been studied granulometric and chemical compositions of the concentrates, their main technological and briquetting properties, reducibility and also carried out test meltings to produce titanium-bearing slag and pig iron. It has been shown, that the "O","Q" and "MK" concentrates, containing 94,71; 91,43 and 95,23% respectively of the total of valuable components - iron oxide and titanium dioxide (balance - impurities) may be processed by electrical melting into titanium-bearing slag (86,89% of TiO_2) and pig iron. Slag was tested as a raw material for the production of titanium tetrachloride; the obtained product by its composition was suitable for a subsequent processing to produce titanium dioxide and titanium metal.

Chapter I

CHEMICAL COMPOSITION OF ILMENITE CONCENTRATE

Three samples of deposits in the states of Orissa ("O" concentrate), Madras (Q concentrate) and Kerala ("MK" concentrate). These concentrates by its appearance are in the form of black free-flowing sandy material with grains of the minerals having a poorly-rounded confuguration. The granulometric composition of the investigated concentrates given in Table I shows, that they relate to fine-grained varieties, the bulk of which (92,34 - 97,55%) is within the particles sise range of - 0,315 +0,10mm.

Table 1

Granulometric analysis of concentrates,%

Particle sizes, in mm	Concentrate "O"	"Q"	"MK"
-0,5 + 0,315	2,35	1,81	4,26
-0,315+0,25	7,69	5,62	9,43
-0,25 + 0,20	21,96	22,33	26,20
-0,20 + 0,16	29,65	36,97	37,11
-0,16 + 0,125	21,78	25,96	19,60
-0,125 + 0,10	11,97	6,67	3,22
-0,10	4,60	0,64	0,18

Mineralogical analysis shows the following composition of the concentrates (Table 2).

Table 2

Mineralogical analysis of concentrates, in %

Minerals		Concentrate		
		"O"	"Q"	"ПК"
a. Titanium-bearing:				
1. Ilmenite		97,08	24,47	53,21
2. Arizonite	moddfied ilmenite	-	60,56	44,99
3. Lencoxene		0,26	8,85	1,04
4. Rutile		-	1,64	0,17
Totally		97,34	95,52	99,41
b. Impurities				
1. Garnet		0,34	0,38	0,26
2. Sillimanite		0,10	1,64	0,22
3. Zircon		-	1,55	-
4. Monazite		-	0,50	-
5. Hematite		1,22	-	-
6. Iron hydroxides		0,37	-	-
7. Balance		0,63	0,41	0,11
Totally		2,66	4,48	0,59
Sum		100	100	100

The other materials are: pyroxenes, mica, spinel, fragments of quarts-bearing rocks.

It has been found by the mineralogical investigations that these concentrate differ both by their content of main minerals and impurities. While the concentrate "O" is mainly in the form of ilmenite (97,08%), then the concentrate "Q" is modified to a considerable extent by physical and chemical processes occurring in the nature. 69,41% of it are in the form of arizonite and leucoxene phases and only 24,47% relate to a residual ilmenite. Among other contaminant minerals, sillimanite, zircon and not unharmful monazite are notable for their higher quantities, 1,64%, 1,55% and 0,50% respectively.

As for the extent of main titanium-bearing mineral oxidation, the "MK" concentrate is between the concentrates "O" and "Q". It is characterized by the hightest content of the total of titanium-bearing minerals (99,41%) and low content of free contaminant minerals (0,59%).

The chemical analysis of the investigated iron-bearing titaniferous concentrates, given in Table 3, shows, that the bulk of the concentrates is the total of iron and titanium oxides: in the "O" concentrate it amounts to 94,71%, in the "Q" - 91,43%, and in the "MK" - 95,24%

The highest quantity of foreign impurities, mainly in the form of alumina, silica and magnesium oxide, is present in the concentrate "Q" (9,60%), and the lowest one in the concentrate "MK" (4,70%).

These data indicate that the investigated concentrates, expect the concentrate "Q" both by the content of main useful components and impurities may be classified as high - grade materials.

The results of mineralogical and chemical analysises show, that the total of impurities in the concentrate "Q" is almost two times that of the concentrate "O" and seven times that of the concentate "MK". Evidently, through technological improvement of the deposit "Q" sands benefication may considerably lower the content of free contaminant minerals, particularly sillimanite,(contaminates the concentrate with alumina and silica) zircon and monizite, which betters the quality of this concentrate and the smelted therfrom titanium-bearing slag.

Thus, on the basis of the possibility to obtain titanium-bearing slags, which contain the highest quantity of titanium dioxide and the lowest quantity of impurities, the tested concentrates may be arranged in the following sequency: "MK" - "O" - "Q".

Table 3

Chemical composition of concentrate, %

Consentrate	TiO_2	FeO	Fe_2O_3	SiO_2	Al_2O_3	CaO	MgO	MnO	Cr_2O_3	V_2O_5	P_2O_5	ZrO_2	S	Nb_2O_5	Tq_2O_5	Annealing losses	Total
"O"	48,95	34,30	11,46	0,76	1,35	0,18	0,18	0,27	0,046	0,20	0,048	-	0,055	0,11	0,005	0,80	99,66
"Q"	58,24	8,80	24,39	1,47	2,70	0,24	1,23	0,17	0,12	0,21	0,196	105	0,036	0,18	0,0072	2,0	101,04
"MK"	54,42	22,62	18,2	0,42	1,29	0,24	1,28	0,15	0,007	0,19	0,079	-	0,38	0,15	0,007	1,2	100,35

Chapter II

PROCESSING OF CONCENTRATES INTO TITANIUM-BEARING SLAG AND PIG-IRON

I. Some technological properties of concentrates

Technological properties of concentrates effect significantly a reducing melting process. The properties, which are the most important for melting, are given in Table 4.

Table 4

Technological properties of indian concentrates

Properties	Unit of measure	Concentrate		
		"O"	"Q"	"MK"
Specific weight	g/cm^3	4,66	4,30	4,49
Bulk weight	"	2,80	2,51	2,69
Shaked bulk weight	"	3,08	2,81	3,05
Initial temperature of sintering	°C	1265	1355	1305
Initial temperature of melting	"	1440	1500	1440
Final temperature of melting	"	1450	1510	1450
Angle of rest	grades	30-31	29-30	29-30
Specific electrical conductivity				
at 20°C	$ohm^{-1}cm^{-1}$	3.10^{-8}	8.10^{-9}	2.10^{-7}
at 1000°C	- " -	$1,3.10^{-1}$	6.10^{-2}	$1,4.10^{-1}$

2. Briquetting properties of concentrates

The practice of running electrical thermal furnace shows, that the processing of iron-bearing titaniferous concentrates in unbriquetted form involves considerable concentrate losses in the form of dust carried away with exhaust gases.

The investigation of briquetting properties therefore was of a much interest, since the briquetting may be one of feasible means of preparing the charge for melting.

A charge of concentrate and a reducing agent were throughly agitated in a dry state followed by the pressing with a binding agent (sulphate-cellulose liquer) having a density of 1,27-1,28g/cm^3 in a vertical hydrolic press at a pressure of 200kg/cm^2. The prepared briquettes, having a diameter of 21 mm and a height of 10-11mm were dried at a room temperature for 20 hours and then at 105°C for 5 hours. After drying the briquetts underwent collapsing strength tests.

The investigations have shown that the maximum strength of briquetts, containing anthracite (200-210kg/cm^2,100-110kg/cm^2 and 120-130kg/cm^2) and made of the concentrates "O", "Q" and "MK" is obtained when the binding agent ammounts to 12,10 and 8 % respectively, based on the concentrate weight.

In the case when petroleum coke is used the best strength of briquetts (150-160kg/cm^2, 100-110kg/om^2 and

130 -140kg/cm²) is obtained, when a binding agent is present in the charge in an amount of 12,14 and 10%. Both the increase and decrease of the amount of a binding agent as against the optimum amount deteriorates the strength of briquetts.

3. Reducibility of concentrate in solid phase

The reduction of iron oxides in the electrical thermal melting process is the primary object of processing.

In connection with this, tests have been carried out to study the reduction of the concentrate in solid phase in relation to temperature and test time.

Anthracite (86,71% of C, 8,23% of ash, 4,13% of volatile matter and 0,66% of moisture), petroleum coke (92,97% of C, 0,72% of ash, 5,13% of volatile and 0,44% of moisture) and commercial hydrogen were used as reducing agents.

To study the effect of the method by which charge is prepared on the reducibility of iron and titanium oxides present in the concentrate there was tested a charge in the form of briqquets and powder containing 10-11% of a reducing agent.

The investigations were carried out in a laboratory installation to study the reducibility of the concentrates; the process was studied in a temperature range of 700-1300°C and at test duration of 0,5-3,0 hours. During the tests, carried out at high temperatures (1100-1300°C) besides to the extent of iron oxides reduction there was also determined the extent of titanium dioxide reduction.

The results of the investigations on the reduction of concentrates in the form of briquetted and pulverulent charges show (Table 5) that an intensive reduction of iron oxides (to 70-81%, 75-86% and 80-89% respectively for the concentrates "O","Q" and "MK") proceeds in a temperature range of 1100-1300°.

Although the process is carried out at sufficiently high temperatures (1200-1300°) during a long period of time (3 hours) and with necessary quantity of a reducing agent, the complete reduction of iron oxides has not been attained. It may be supposed that in these conditions the primary slag-forming reactions start and the process extends into the diffusion region, where the rate and extent of the reaction is determined by the rate of diffusion of a reducing agent and a gaseous reaction product.

The analysis of the briquetted and pulverulent charge reduction reveals that along with the reduction of iron oxides at high temperatures (1200-1300°C) takes place also the reduction of titanium dioxide to lower oxides.

Table 5

Reducibility of indian ilmenite concentrates

Concentrate

	Reducing agent-solid carbon				Gaseous reducing agent (H_2)	
	Briquetes with anthracite	Briquettes with petroleum coke	Powder with anthracite	Powder with petroleum coke	Powder	
Temperature °C	Time - 2 hours				Temperature °C	Time - 1 hour
1000	not found	0,4	1,3	0,7	700	37,3
1100	54,7	16,0	2,8	2,6	800	70,4
1200	65,7	78,0	82,4	79,4	900	83,2
1300	68,9	49,0	79,5	85,0	1000	85,7
Time in hours	Temperature - 1200°C				Time in hours	Temperature 1000°C
0,5	68,7	53,0	56,4	46,5	0,5	76,5
1,0	79,1	73,2	66,0	53,8	1,0	85,7
2,0	85,7	78,0	82,4	79,4	2,0	89,3
3,0	80,9	79,0	78,0	73,6	3,0	91,5

Concentrate "Q"

Temperature °C	Time - 2 hours				Temperature °C	Time - 1 hour
1000	0,91	2,3	2,2	6,5	700	66,7
1100	25,0	17,7	26,8	20,3	800	90,6
1200	79,8	60,0	70,0	75,6	900	88,6
1300	75,4	79,6	68,5	60,6	1000	76,9

Time in hours	Temperature - 1200°C				Time in hours	Temperature 1000°C
0,5	13,0	25,8	12,3	6,9	0,5	82,0
1,0	21,1	32,6	62,6	13,4	1,0	76,0
2,0	79,8	60,6	70,0	75,6	2,0	82,0
3,0	86,1	77,9	70,5	76,0	3,0	81,0

C o n c e n t r a t e " MK "

Temperature °C	Time - 2 hours				Temperature °C	Time - 1hour
1000	3,2	15,8	0,5	0,97	700	54,0
1100	64,0	43,5	62,4	35,0	800	76,3
1200	76,3	79,4	80,5	78,0	900	88,3
1300	88,7	86,5	80,7	78,8	1000	84,5

Time in hours	Temperature -1200°C				Time in hours	Temperature
0,5	43,5	37,3	49,0	56,0	0,5	80,7
1,0	60,5	62,6	74,0	67,3	1,0	85,4
2,0	76,3	79,4	80,5	78,0	2,0	86,2
3,0	74,0	74,5	74,6	74,6	3,0	88,8

The extent of titanium dioxide reduction at these temperatures attains 10-12%, 7-17% and 7-8% respectively for the concentrates "O","Q" and "MK".

When the concentrate is reduced with a gaseous reducing agent (hydrogen) the rates of the process sharply increase even at 700°C and the duration of 1 hour, the extent of reduction of iron oxides present in the concentrates "O","Q" and "MK" in a tube furnace amounted to 37,67 and 54% and with further temperature increase it attained 91,82 and 89% respectively.

This indicates that the use of gaseous reducing agents provides significant advantages due to first of all high reactivity of gas and a large surface of contact between pulverulent concentrate and gaseous reducing agent.

In the light of an eventual development and introduction into production of the reduction processes in a boiling bed there was studied a feasibility to reduce concentrates in a laboratory boiling bed single-chamber reactor with hydrogen. The tests were carried out at temperatures of 700,800,900 and 1000°C. It has been found that it is possible to treat in a pseudo-fluidized state only the concentrate "Q" (the extent of iron oxides reduction amounted to 91% at a temperature of 900°C and the duration of 1 hour), while the concentrates "O" and "MK" began to sinter and transformed into a complete monolith even at temperatures of 800 - 900°C for inicial 0,25 - 0,50 h of their presence in the bed.

Thus, the carried out tests showed, that the investigated concentrates can be reduced in a solid phase (approximately by 80% at 1200°C with the use of the most available reagents - anthracite and petroleum coke.

4. Reducing melting of concentrates to produce titanium-bearing slag and pig-iron

The primary technological object of melting comprises the seperation iron and titanium, contained in the concentrate , resulting in the two individual products of their own specific weights and in the form of unmiscible layers (metal and titanium-bearing slag. On the basis of the chemical annlysis of the concentrates preliminary evaluation of slag and metal composition was made by means of a theoretical calculation of iron-bearing titaniferous concentrates reducing melting. Such a calculation was carried out with some assumptions based on a rich experience in producing slag with high titanium and low iron content in the U.S.S.R.

The make-up of melting balance and the calculation of a required quantity of a reducing agent for the charge was based on the necessity to produce titanium-bearing slag with 3-4% of FeO and the following coefficients of the concentrate components distribution between slag and metal:

silica, chrome, vanadium and manganese oxides are reduced by 20% and pass into the metal, and magnesia, alumina, calcium and zirconium oxides remain completely in the slag. As melting proceeds titanium dioxide is reduced to lower oxides, primarily to Ti_2O_3, approximately by 40-50% and together with the remained unreduced oxides of other metals make up the base of titanium-bearing slag. Similar assumptions are made for anthracite ash.

According to the carried out metallurgical calculations (Table 6) it has been found, that reducing melting of the investigated concentrates requires reducing agent, amounting to 10-11% bassed on the concentrate weight.

Laboratory investigations on the technological testing of ilmenite concentrates were carried out in a 28kwA single-phase electric melting furnace (rf. figure). An electric furnace was provided a conductive graphite hearth, its bath was lined with a magnesite brick and had inside a graphite ring with a diameter of 120mm to prevent slag from interacting with a refractory material. A furnace was provided with a graphitized electrode, having a diameter of 70mm and operated in the following electric regime: voltage - 20V; amperage - 1360 A with the fluctuations of ± 200A.

The crushed anthracite, containing 36,71% of carbon and 8,23% of ash was used as a reducing agent through for

Table 6

Calculated material balance of titanium-bearing slag melting from indian ilmenite concentrates

Charged, kg				Produced, kg						
Concentrate		Anthracite	Totally	Slag			Pig iron			Gases - Losses
				con-sumption	kg	%	Consumption	kg	%	kg
Concentrate "O"										
Totally	100	11,219	111,219	Totally	53,406	100,0	Totally	34,535	100,0	23,278
including										
TiO_2	48,95	0,05	49,0	TiO_2	47,29	88,55	Ti	0,25	0,72	1,46
Fe_2O_3+FeO	45,76	0,21	45,97	FeO^2	1,8	3,37	Fe	33,58	97,23	10,59
Balance	5,29	10,959	16,249	Balance	4,316	8,08	Balance	0,705	2,05	11,228
Concentrate "Q"										
Totally	100	10,623	110,623	Totally	65,067	100,0	Totally	24,063	100,0	21,493
including										
TiO_2	58,24	0,041	58281	TiO_2	56,32	86,55	Ti	0,23	0,95	1,731
Fe_2+FeO	33,19	0,172	33,362	FeO^2	1,238	1,91	Fe	23,089	93,96	9,035
Balance	8,57	10,410	18,98	Balance	7,509	11,54	Balance	0,744	3,09	10,727
Concentrate "MK"										
Totally	100	10,444	110,444	Totally	58,049	100,0	Totally	28,248	100,0	24,147
including										
TiO_2	54,42	0,736	54,736	TiO_2	52,805	90,96	Ti	0,31	1,09	1,621
Fe_2 + FeO	40,82	0,23	41,05	FeO^2	1,61	2,77	Fe	27,44	97,13	12,0
Balance	4,76	9,898	14,658	Balance	3,634	6,27	Balance	0,498	1,78	10,526

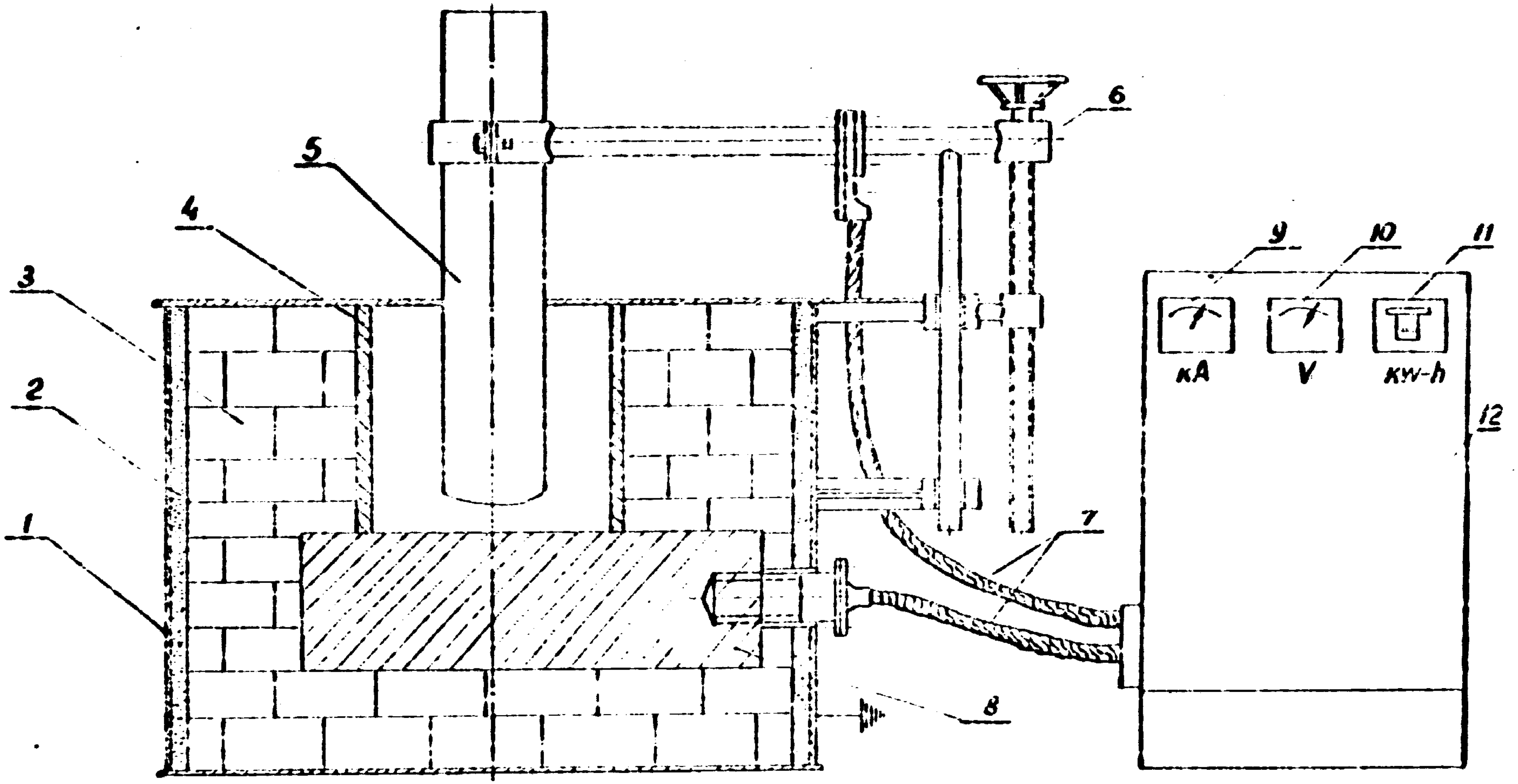
these purpose petroleum coke may be also used. Due to the fact that test meltings were carried out in a laboratory furnace and a part of carbon burnt out in the furnace tops, the amount of a reducing agent, introduced into the charge, was 1,5 times the calculated amount required for a complete reduction of iron oxides to metal and titanium dioxide to Ti_3O_5.

The concentrates were melted by a batch process, which provided the melting of batches of pulverulent charge, made up of the mixture of the concentrate and a solid reducing agent. Usually 2-3kgs of charge were processed for 1 melting operation. The melted products were discharged from the furnace and processed into titanium-bearing slag and pig-iron. The obtained slag was crushed and magnetically seperated from the coarse-grained inclusions of iron metal.

The average samples of titanium-bearing slag and pig-iron taken from several melts were chemically analysed.

On the basis of the obtained data for the yield of slag and metal and their chemical composition (Tables 7 and 8) there has been made up a material balance for the melting of either of the investigated concentrates (Table 9).

The test melting showed, that the slag yield attained in the processing of the concentrates "O","Q" and "MK" amounts to 52-53, 64-65 and 58-59% based on the weight of the concentrate being melted, and the pig-iron yield - 33-34,



28 kwa laboratory arc furnace (1- jacket, 2- filler, 3- magnesite lining, 4- graphite cylinder, 5- graphite electrode, φ 80mm; 6- lifting mechanism, 7- leads, 8- conductive bottom plate, 9- ammeter, 10- voltmeter, 11- power consumption counter, 12- 28 kwa transformer).

24-25 and 28-31% respectively.

The supervision over the course of meltings allowed to find out that these concentrates may be processed into titanium-bearing slag and pig-iron by the method of reducing melting in electrical thermal furnaces.

The concentrates "Q" and "[illegible]" were particularly good for melting, while the processing of the concentrate "O" showed a relativo instable electrical behaviour of melting due to a high content of iron oxides and a relatively low content of slag-forming impurities present in the concentrate.

These facts made for a high electrical conductivity and the furnace electrodes work in specified are operational conditions. To better the processing conditions for the concentrate there were carried out. meltings with the addition of the concentrate "Q", their ratio being 1:1. This series of meltings "proceebls normally without pulsating power load.

As for the composition and the quality of the products obtained by reducing melting of the indian concentrates it should be noted the following.

Firstly, titanium-bearing slags, smelted from all the three ilmenite concentrates are characterized by a rather high content of main component (86,1-89,4% calculated as TiO, slag rereduced to lower titanium oxides not counted and a relatively low content of other metals oxides.

The slag contain usually 14-26% of Ti_2O_3 and 14-23% of TiO_2. In the case when titanium lower oxides are calculated as TiO_2, the content of TiO_2 in the slag increases by 2-3%

Table 7

Composition of titanium-bearing slag smelted from indian ilmenite concentrates,%

Concentrate	TiO_2	FeO	$Fe_{metallic}$	SiO_2	Al_2O_3	CaO	MgO	MnO	Cr_2O_3	ZrO_2	V_2O_5	P_2O_5	Total
"O"	88,04	3,0	0,61	1,93	2,40	0,59	2,43	0,49	0,044	-	0,25	0,016	99,80
"Q"	86,1	2,54	0,65	2,13	3,74	0,51	1,95	0,38	0,094	1,57	0,22	0,021	99,90
"MK"	89,40	2,87	0,54	1,68	2,13	0,58	1,87	0,36	0,067	-	0,24	0.015	99,75
"O"+"Q"=1:1	87,15	2,83	0,60	1,65	3,22	0,57	2,34	0,40	0,063	0,84	0,21	0,027	99,90

* The slag by ots content of TiO_2 is present in the form of the total of all titanium oxides (TiO_2+ Ti_2O_3 + TiO). In the case, when titanium lower oxides are calculated as titanium dioxide, its concentration increases by 2,0 - 3,0%.

Table 8

Composition of pig-irons, produced in melting indian ilmenite concentrates,%

Concentrate	C	Si	Cr	Mn	Ti	V	Ni	P	S
"O"	0,934	0,54	0,070	0,29	1,40	0,21	0,025	0,021	0,096
	0,972	0,19	0,037	0,15	0,74	0,084	0,030	0,021	0,142
	0,491	0,047	0,026	0,038	0,082	not found	0,015	0,034	0,216
Averaged	0,8	0,26	0,26	0,16	0,74	0,147	0,023	0,025	0,151
"Q"	2,87	0,28	0,11	0,096	0,45	0,11	0,027	0,315	0,104
	3,36	0,17	0,12	0,092	0,34	0,115	0,025	0,31	0,075
	3,37	0,55	0,15	0,171	0,91	0,20	0,034	0,34	0,83
Averaged	3,2	0,33	0,126	0,12	0,9	0,141	0,028	0,321	0,087
"MK"	2,88	1,03	0,089	0,16	1,58	0,18	0,024	0,077	0,096
	1,88	0,09	0,045	0,030	0,15	0,04	0,029	0,061	0,233
	3,20	0,85	0,12	0,23	1,77	0,25	0,030	0,080	0,089
Averaged	2,65	0,66	0,085	0,14	1,17	0,16	0,028	0,079	0,139
"O" +"Q"=1:1	2,25	1,32	0,155	0,25	2,26	0,29	0,026	0,100	0,096

Actual material balance for smelting titanium bearing slag from indian ilmenite concentrates

	Charged, kg			Produced,						
	Concentrate	Anthracite	Totally	Slag			Pig - iron			
				Composition	kg	Yield%	Composition	kg	Yield,%	kg
Concentrate "O"										
Totally	10,55	1,714	12,264	Totally	5,56	52,7		3,54	33,6	3,164
including										
TiO_2	5,16	0,07	5,167	TiO_2	4895	88,04	Ti	0,026	-	0,246
Fe_2O_3+FeO	4,83	0,031	4,861	FeO	0,167	3,0	Fe	3,46	-	1,234
Balance	0,56	1,676	2,236	Balance	0,498	8,96	Balance	0,054	-	1,681
Concentrate "Q"										
Totally	6,245	1,109	7,354	Totally	4,01	64,2		1,54	24,6	1,804
including										
TiO_2	3,64	0,005	3,645	TiO_2	3,452	86,1	Ti	0,014	-	0,179
Fe_2+ FeO	2,07	0,02	2,09	FeO	0,102	2,54	Fe	1,46	-	0,528
Balance	0,535	1,084	1,619	Balance	0,456	11,36	Balance	0,066	-	1,097
Concentrate "MK"										
Totally	6,0	1125	7,125	Totally	3,51	58,5		1,896	31,6	1,719
including										
TiO_2	3,26	0.005	3,265	TiO_2	3,14	89,4	Ti	0,022	31,6	0,103
Fe_2O_3 + FeO	2,45	0,02	2,47	FeO	0,101	2,87	Fe	1,80	-	0,569
Balance	0,29	1,10	1,39	Balance	0,269	7,73	Balance	0,074	-	1,047

Note: Slag and pig-iron yields are given in weight %, based on concentrate being smelted due to which the total of slag components increases up to 102 -103%.

Titanium-bearing slags, which are of the highest grade by their composition, are produced from the concentrates "MK" and "O", and those of somewhat lower grade - due to higher content of contaminant alumina (about 4%) and silica (above 2%) - from the concentrate "Q".
It will be understood, that the improvement of the concentrate"Q" benification technology with a view of lowering their content of SiO_2, Al_2O_3 and ZrO_2 may assure the smelting of slags therefrom containing 88-90% of TiO_2.

Secondly, pig-irons produced in the melting of the concentrates contain such alloying elements as chrome (0,02(- 0,15%), manganese (0,10 - 0,20%), vanadium (0,10 - 0,30%), silicon (o,20-1,0%) and highor titanium quantity (0,20-1,50%) as against the usual smelted pig-irons, which is evidently due to some rereduction of slag (the formed titanium carbide could dissolve in pig-iron). The most specified feature of pig-iron particularly the pig-irons, smelted from the concentrate "Q" is their relatively high content of sulphur (0,10-0,20%) and phosphorus (0,10-0,30%), which are carried into the melt mainly with the concentrate and anthracite.

More through purification of the concentrates and the use of purer materials, of far as the content of these components is concerned, as a reducing agent (for example, petroleum coke, etc.) enables to obtain pig-irons from the indial concentrates, those pig irons containing sulphur and phosphorus 3-5 times as little, which consequently betters the quality of the smelted pig-irons.

Otherwise, a special additional treatment is required to refine them from these harmful impurities, which may be carried out by one of the known methods of ferrous [illegible].

Taking into consideration a high yield of pig-iron in the melting of the indian concentrates (0,64;0,57 [illegible] 0,[illegible]/t of slag) it may be said its marketing as a commercial product allows to considerably better technical and economical ratings of titanium-bearing slag production.

Crystallooptical investigations of the smelted slags showed, that their phase composition met the requirements for conventional titanium-bearing slags. The bulk of slag is in the form of anosowite. There may be observed small quantities of ilmenite (in the form of thin fringes around the anosowite grains), glassy material and iron metal in the form of solitary reguli.

It is possible to obtain titanium tetrachloride followed by titanium dioxide pigment or titanium metal from the smelted titanium-bearing slags by any known industrial method.

After special treatment carried out with a view of giving an easily sulfuric acid-leached crystal structure (quenching) to the slags they may be used as a raw material to produce titanium dioxide by the sulfuric acid method as well.

Thus, the investigations carried out in laboratory conditions showed, that it is possible to produce two products from the indian ilmenite concentrates by the method of reducing melting with the use of conventional solid reducing agents (anthracite and also petroleum coke, young gas coals, etc.); these two products being titanium - bearing slag and pig-iron either of which may be marketed as a commercial product.

The organisation of the industrial processing of the indian ilmenite concentrates according to the developed in the USSR flow sheets for obtaining high titanium-bearing slag and pig-iron may assure the following tentative main readings for the melting process to produce titanium-bearing slag and pig iron:

1. Titanium dioxide recovery from concentrate into slag - 96%.

2. Composition of the concentrates "O", "Q" and "MK" per 1 t of natural slag - 1,91; 1,60 and 1,80t respectively.

3. Power consumption in the melting of the concentrates "O", "Q" and "MK" per 1 t of natural slag - 3500-3700; 2300-2500 and 2600-2800 kwth respectively.

4. Reducing agent consumption - 0,140, 0,125 and 0,125; 0,200 and 0,225 per 1 t of natural slag.

5. Consumption of graphitised electrodes per 1 t of slag - 0,030 - 0,040t.

6. Pig-iron yield per 1 t of slag smelted from the concentrates "O","Q" and "MK" - 0,64, 0,37 and 0,45t.

Chapter III

Production of titanium tetrachloride

Titanium-bearing slag smelted from the indian concentrates "O", "Q" and "MK" in a large -sized laboratory installation after magnetical seperation were mixed with petroleum coke, coal-tar pitch and sulfite-cellulose liquor in proportions approximate to those used conventionally in industrial processing.

Thus prepared charges were briquetted in a laboratory hydrolic press III-10 at a pressure of 230kg/m^2 after which the briquetts were dried in a drying cabinet at a temperature of 100-120°C and coked at 800°C to remove hydrocarbons. The composition of the coked briquetts is given in Tabele 10.

Table 10

Composition ofb coked slag briquetts,%

Slag	TiO_2	FeO	Al_2O_3	SiO_2	CaO	MgO	MnO	Cr_2O_3	ZrO_2	V_2O_5	C
"O"	69,17	2,45	1,82	1,47	0,45	1,85	0,24	0,04	0,06	0,18	24,0
"Q"	69,16	3,29	2,16	1,62	0,39	1,48	0,29	0,09	0,05	0,17	24,3
"MK"	68,92	2,39	1,67	1,27	0,44	1,72	0,31	0,07	0,09	0,13	23,3

The chlorination was carried out in a laboratory installation somewhat simulating industrial processing installations.

The process was carried out at a temperature of 800-900° chloride consumption was within the limits of 650-600 l/h. The briquetts made of the slag "O" were chlorinated during 8 hours, the briquetts of "Q" - 7 hours and the briquetts of "MK" - 6 hours.

The composition of the obtained commercial titanium tetrachloride and the overall composition of the chlorination products are given in Tables 11 and 12.

Table 11

Overall composition of solid chlorides /in weight,%/

Slag	$AlCl_3$	$FeCl_3$	$FeCl_2$	$ZrCl_2$	Mn Cl_2	Mg Cl_2	Ca Cl_2	Cr Cl_2
"O"	24,80	26,80	5,40	11,80	3,40	22,80	4,50	0,40
"Q"	30,80	23,80	6,20	12,20	2,80	19,10	4,20	0,80
"MK"	24,70	28,60	5,40	12,90	2,80	19,60	5,10	0,60

Table 12

Impurities content of a commercial titanium tetrachloride (in weight %)

Slag	VO Cl_2	Fe	Mn	Cr	Si	Sn	Al
"O"	0,142	0,042	0,002	0,0005	0,012	0,001	0,001
"Q"	0,170	0,0015	0,002	0,005	0,010	0,001	0,003
"MK"	0,126	0,001	0,002	0,005	0,11	0,001	0,001

Table 13

Chemical composition of residue (in weight %)

Slag	TiO_2	FeO	SiO_2	Al_2O_3	CaO	MnO	Cr_2O_3	ZrO_2	V_2O_5	C	$CaCl_2$
"O"	9,9	0,18	14,3	0,32	0,31	0,35	0,03	0,11	0,03	52,7	21,3
"Q"	5,8	0,26	13,9	0,38	0,27	0,21	0,03	0,12	0,03	60,2	16,8
"MK"	7,5	0,63	15,2	0,34	0,20	0,21	0,06	0,06	0,03	56,5	17,3

Table 14

Material balance for chlorination of titanium-bearing slags, smelted from concentrates "O","Q" and "MK"

Balance item	"O"		"Q"		"MK"	
	g	%	g	%	g	%
Charged:						
Coked briquetts	1374	42,8	1293	41,7	1257	43,3
Chlorine	1762	57,2	1807	58,3	1647	56,7
Totally	3076	100	3100	100	2884	100
Produced:						
Commercial titanium tetrachloride	1793	58,2	1800	58,1	1799	59,0
Solid chloride of dust chambers	31,0	1,0	31,5	1,0	29,5	1,0
Condensed pulp	366,0	12,0	376,0	17,4	368,0	14,0

Table 15

Titanium material balance

Name of product	Quantity			Titanium content /in weight % /			Titanium quantity		
	"O"	"Q"	"MK"	"O"	"Q"	"MK"	"O"	"Q"	"MK"
Briquetts	1314	1293	1237	40,69	40,68	40,50	534,7	526,0	501,5
Totally	1314	1293	1237	-	-	-	534,7	526,0	501,5
P R O D U C E D									
T i t a n i u m tetrochloride (commercial	1793	1800	1709	24,82	24,80	24,85	445,0	447,0	426,0
Solid chlorides in dust chambers	31,0	31,5	29,5	0,23	0,16	0,053	0,071	0,05	0,02
Condensed pulps	366	376	368	12,41	12,38	12,52	45,50	46,50	44,80
Solid chloride in heat exchangers	47,70	49,30	46,00	7,79	7,25	13,74	3,72	3,6	6,32
Exhaust gases	476	607,5	452	4,06	3,70	2,54	19,37	22,5	11,5
Unchlorinated residue	362	236	279	5,81	3,42	4,42	21,03	6,07	12,36
Totally	-	-	-	-	-	-	534,7	526,0	501,5

Table 14 shows the overall material balance of chlorination process, where the quantity of consumed chlorine is calculated from the actually obtained titanium tetrachloride and solid chlorides, counting chloride losses carried away with exhaust gases as hydrogen chloride. The latter value was determined counting the content of HCl in exhaust gases of industrial enterprises. The quantity of exhaust gases was calculated from the proportions of CO and CO_2. in exhaust gases and quantity of consumed hydrocarbon.

According to the overall balance (Table 14) chemical composition of starting and final chlorination products (Table 10-12) there has been determined the titanium material balance (Table 15) and calculated the consumption coefficients (Table 16 of the yield of main chlorination products.

Table 16

Main consumption coefficients in tons per 1 t of titanium tetrachloride (tentative)

Slag Briquetts		Chlorine[x]	Copper powder or	Hydrogen sulphide	Coke	Sulphite liquor	Coal-tar pitch
"O"	0,735	0,95-1,05	0,005-0,006	0,005	0,240	0,075	0,020
"Q"	0,715	0,95-1,05	0,005-0006	0,005	0,240	0,075	0,020
"MK"	0,715	0,95-1,05	0,005-0,006	0,005	0,240	0,075	0,20

x- chlorine consumption is assumed without the utilization of chlorine, contained in solid chlorides.

According to the components content of starting briquetts and unchlorinated residue there has been calculated the extent of chlorination of titanium (96-98%), silica (80-84%), aluminium (93-96%) and iron (93-97%).

The chlorination extent of all the other components is rather high and evidently amounts to as low as 99%.

The yield of solid chlorides in the chlorination of the "O","Q" and "MK" is given in Table 17.

Table 17

Yield of solid chloride in tons per 1t of purified titanium tetrachloride (tentative)

Product	Name of slag		
	"O"	"Q"	"MK"
Solid chlorides	120-130	130-140	120-130
Unchlorinated residue	40 - 80	40 - 80	40 - 80

The purification of a commercial titanium tetrachloride from vanadium oxychloride and the dissolved in the liquid light-valotile impurities and gases gives pure titanium tetrachloride suitable for the production of titanium metal and titanium pigment.

Chapter IV

Conclusion

1. The indian ilmenite concentrates "O","Q" and "MK" obtained for technological testing in laboratory conditions by their granulometric composition are in the form of fine-grained, free-flowing material, the bulk of which (92-97%) is within the particle size range of -315 +0,10mm. As for their mineralogical composition the concentrates differ both by the content of main minerals and impurities; 97% the concentrate "O" is ilmenite and the concentrate "Q" is oxidized to a considerable extent and almost 70% of it is in the form of arizonite and leucoxene phases. By the extent of oxidation the concentrate "MK" is between the unmodofied concentrate "O" and considerable pxidized concentrate "Q".

2. The base of the investigated concentrates is the total of iron and titanium oxides (91-95%). The highest quantity of foreign impurities, mainly in the form of alumina, silica and magnesium oxide in present in the concentrate "Q" (9,60%) and in the concentrates "O" and "MK" their quantities are somewhat lower (5,29 & 4,76% respectively)

These data show, that it is necessary to improve the benefication technology of the deposit "Q" titanium-bearing sands with a view of obtaining concentrates having a lower content of alumina,silica, magnesium and zirconium oxides.

The specific weight of the concentrates varied from 4,30 to 4,66g/cm^3, and the bulk weight from 2,51 to 2,80g/cm^3. The concentrates sinter at temperatures of 1265-1355°C and melt in the range of 1450-1500°C.

3. The concentrates are readily briquetted with a solid reducing agent (anthracite and petroleum coke) with the use of sulphite-cellulose liquor as a binding agent, the consumption of which amounts to 8-12% based on the concentrate weight.

4. The investigations of the concentrates reduction in solid phase showed, that a high reduction extent of iron oxides, present in the concentrate (up to 81-89%) may be attained at temperatures 1100-1300°C in the case of anthracite and petroleum coke used as a reducing agent, and in the case of hydrogen the extent of reduction amounts to 85-88% at 900-1000°C.

5. It hasbeen found, that the reducing melting of the indian ilmenite concentrates gives titanium-bearing slag of a satisfactory quality (86-89% of TiO_2), the rest is the total of iron and contaminant metals oxides) which may be used for the production of titanium tetrachloride. Pig-irons, obtained in the melting of concentrates after the refinement may be also marketed as a commercial product or processed into ferro-aluminium, steel, etc.

6. The organization of industrial processing of ilmenite concentrates according to the developped in the USSR flow-sheets for obtaining high titanium-bearing slags (88-90% of TiO_2) may assure the following ratings:

a) titanium dioxide recovery from concentrate into slag - 96%.

b) consumption of the concentrates "O", "Q" and "MK" per 1 t of natural slag - 1,95; 1,60 and 1,30t respectively.

c) power consumption for the melting of the concentrates "O","Q" and "MK" per 1 t of natural slag - 3500-3700, 2300-2500 and 2600-2800 kwth respectively.

d) reducing agent consumption (anthracite) per 1t of concentrate - 0,140; 0,125 and 0,125t or 0,275; 0,200 and 0,225t/t of slag.

e) consumption of graphitised electrodes per 1t of slag - 0,030-0,40t.

f) pig-iron yield per 1t of slag, smelted from the concentrate "O","Q" and "MK". - 0,64; 0,37 and 0,49 t respectively.

7. Tests carried out for the chlorination of the slags, obtained from the indian concentrates "O","Q" and "MK" showed that the investigated slags are similar by their nature and suitable for the production therefrom titanium tetrachloride by the chlorination method according to the developped in the USSR procedure, assuring satisfactory technical and economical ratings.

8. According to the results of laboratory technological testing there have been determined tentative consumption coefficients of chlorine copper powder (or hydrogen sulphides) coke, etc. and also yield of main products per 1t of

purified titanium tetrachloride which may be used for a preliminary technical and economical evaluation of these kinds of raw materials.

In the industrial processing of the slags "O","Q" and "LK" the tentative recovery of titanium from coked briquetts into purified titanium tetrachloride should be expected at the level of 92% and chlorine consumption per 1t of titanium, tetrachloride amounts to 0,95 - 1,05t. When provisions are made to utilize chlorine, contained in chloride waste products and exhaust gases, chlorine composition may be correpondingly lowered.

Purified titanium tetrachloride may be used for the production of titanium dioxide pigment and titanium metal.

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