MINISTRY OF NATURAL RESOURCES AND ENVIRONMENT OF THE RUSSIAN FEDERATION
FEDERAL AGENCY OF MINERAL RESOURCES

Development of technologies for processing ocean ore from the Russian Exploration Area

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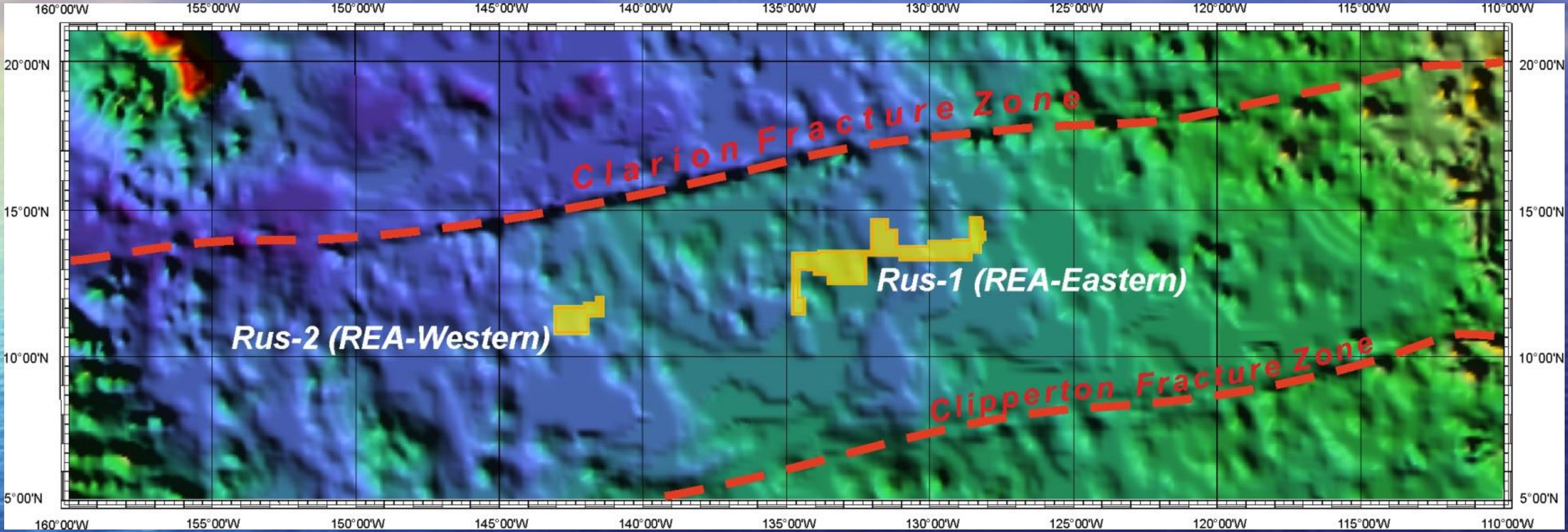
3 - 5 September 2018, Warsaw

The Russian Exploration Area (REA-PMN)



The Russian Exploration Area (REA-PMN), which is 75,000 km^2, incorporates two territories: an Eastern territory (61,600 km^2) and a Western territory (13,400 km^2).

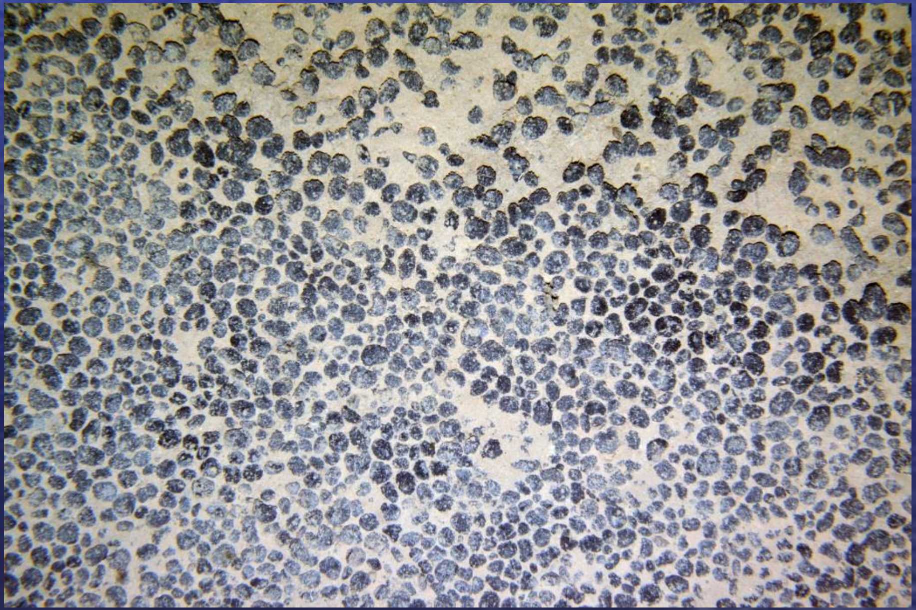
The average concentrations of commercially valuable components in the nodule ore of the REA add up to (%): nickel – 1.39; copper – 1.1; cobalt – 0.23; manganese - 29.3

The processing technologies for polymetallic nodules

The contractor Yuzhmorgeologya started R&D for processing technologies for polymetallic nodules in the period of his acting status of the Pioneer Investor.

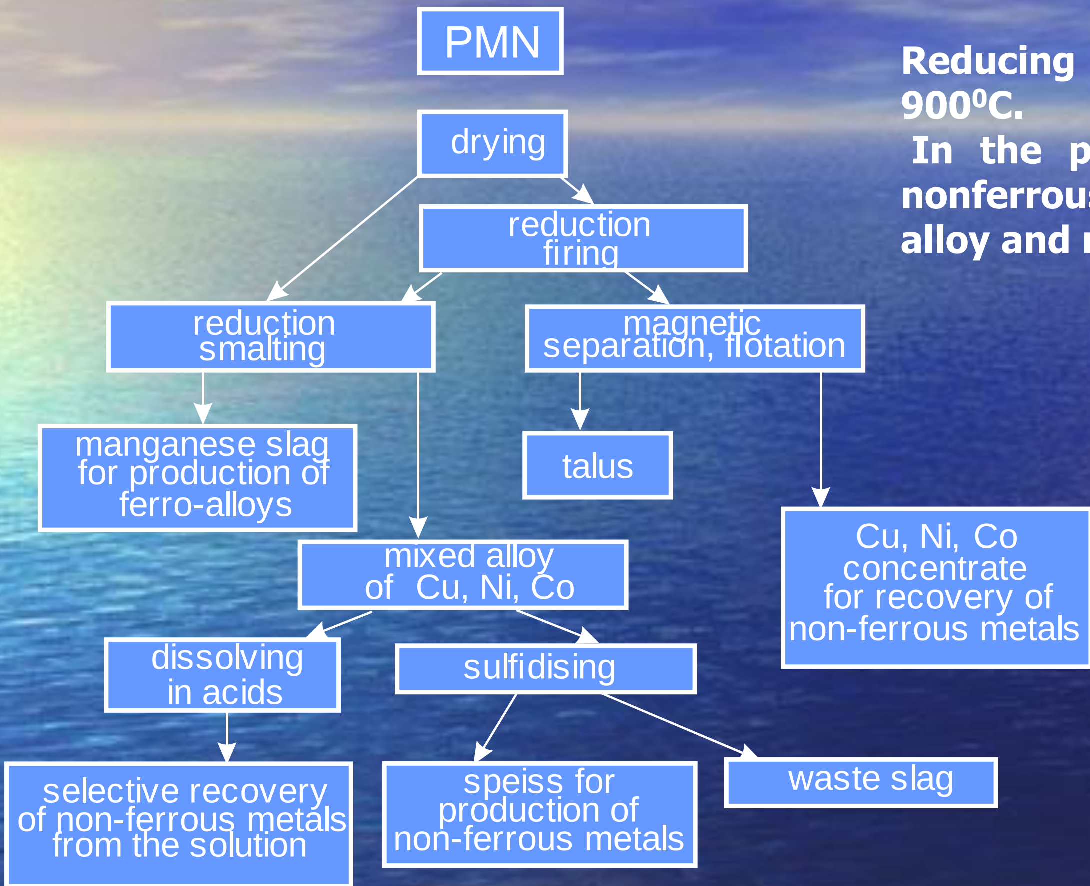
The developed technological schemes can be divided into the main methods:
- pyrometallurgical,
- hydrometallurgical.

Nodule in the cross-section



Nodules in natural occurrence

The pyrometallurgical methods processing



Reducing firing is carried out at a temperature of 800-900^{0}C.

In the process of reduction electrosmelting, 98% of nonferrous metals and up to 90% of iron pass into the alloy and manganese is concentrated in the slag.

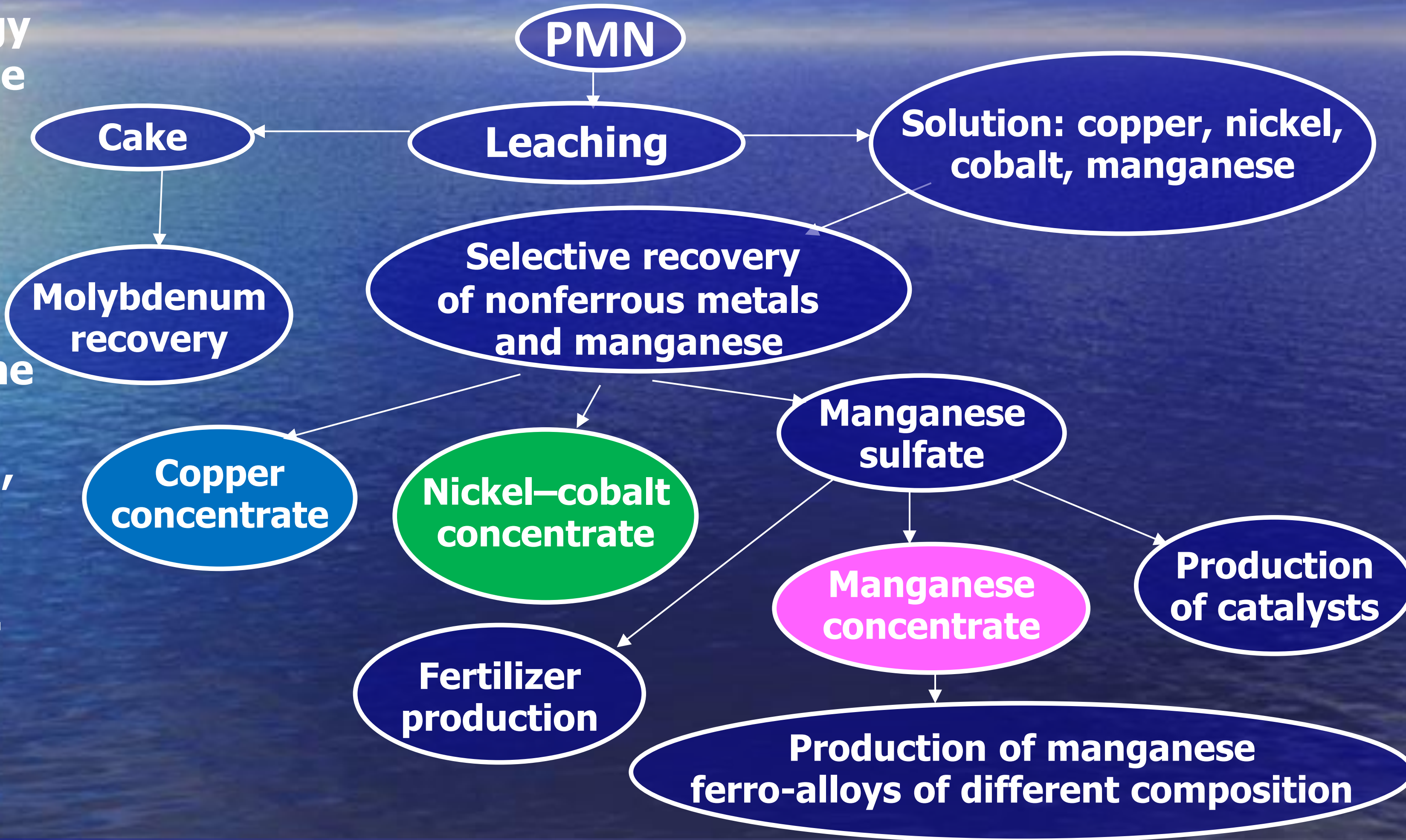
The output of alloy is 6-8,5% with the content of valuable components in the following percent: nickel 12,6-21,0; copper 8,5-11,5; cobalt 2-3; iron 60-70; manganese 0,3-6,0. The output is 72-80% of the primary ore mass with the concentrations of manganese as follows: 39-44 %; nickel 0,01-0,03 %, cobalt 0,01 %, copper 0,02%, the silicon dioxide 12-30%; the calcium oxide 4-10 %; aluminum oxide 5-15 %; and phosphorus oxide 0,02-0,03 %.

Recovery of metals by pyro-metallurgical technology is (%)
Ni - 90; Cu - 88; Co - 86; Mn – 74.

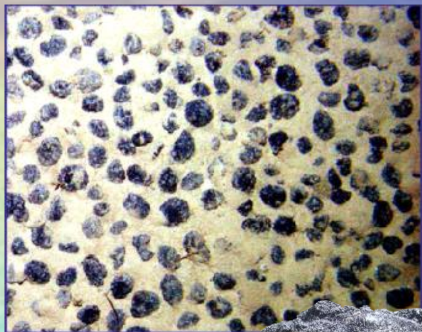
A disadvantage of the process is that it requires high energy consumption in connection with the necessity for drying and aggregation of the entire mass of primary material and also the low content of manganese in the converted slag.

Technological scheme of hydrometallurgical processing of polymetallic nodules

The technology is based on the selective dissolution of non-ferrous metals and manganese, followed by the extraction of copper, nickel, cobalt and manganese from solution. Also molybdenum and zinc are recovered.



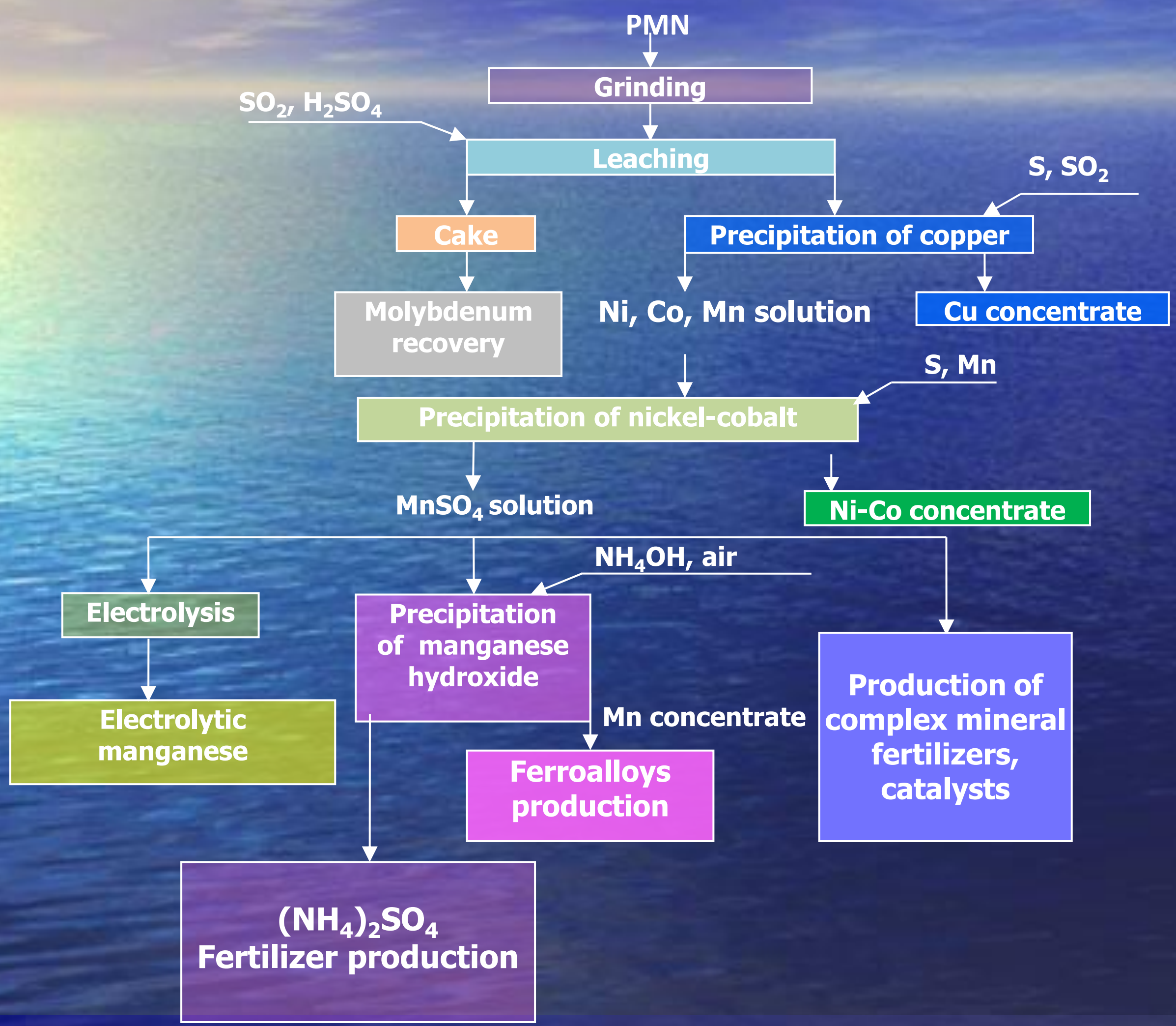
Hydrometallurgical processing



The key operation of the complex processing of polymetallic nodules is their leaching by the solutions of acids in the presence of reducing agents (SO_2, Fe^{2+} and others).

Leaching is carried out by waste gas coming from the combustion of sulfur or by firing of the pyritic concentrates, containing 8-12 % of sulfurous anhydride. In the process of leaching manganese, copper, nickel and cobalt, 95-98 % of them form sulfates that go into solution, from which they are extracted by the sequential precipitation of copper sulfides and nickel-cobalt.

Hydrometallurgical sulfuric technology



The precipitation was carried out at atmospheric pressure by elemental sulfur powders under recovering conditions. Manganese metal was used as a reducing agent in the precipitation of nickel - cobalt. The use of metal manganese and elemental sulfur as reagents eliminates the contamination of sulfate manganese solutions with foreign impurities and provides the possibility of effective utilization of sulfur and manganese regeneration in the process of further processing of the obtained products.

The conceptual scheme of hydrometallurgical processing of polymetallic nodules

A method of copper precipitation from a complex solution is proposed.

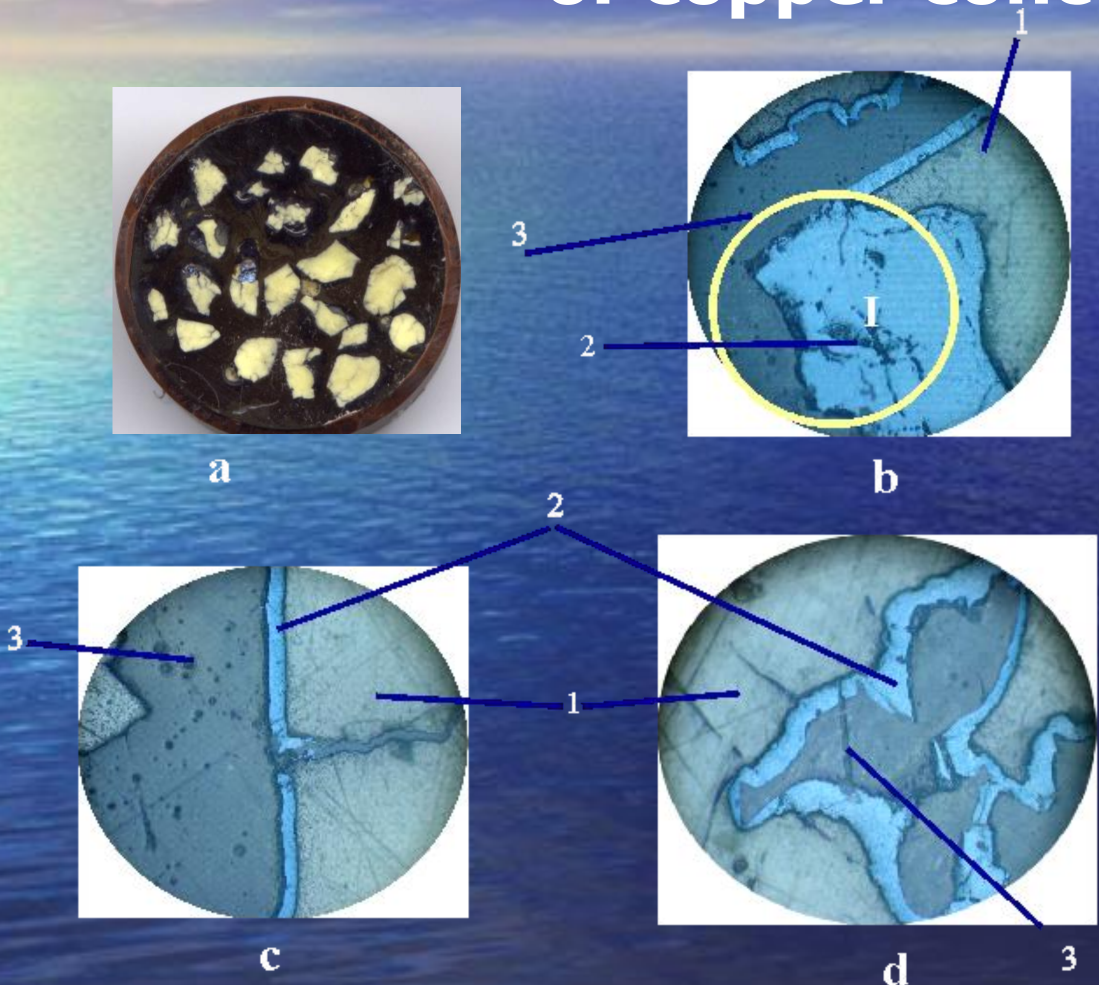
The essence of the proposed method consists in the precipitation of copper powder of elemental sulfur in the presence of a reducing agent – sulfur dioxide. In this case, the following reactions may occur:

$$2CuSO_4 + S^0 + 2SO_2 + 4H_2O = Cu_2S + 4H_2SO_4 \quad (1)$$

$$CuSO_4 + SO_2 + S + 2H_2O = CuS + 2H_2SO_4 \quad (2)$$

Also the formation of low-soluble double salt of copper- $Cu_2SO_3*CuSO_3*2H_2O$

General view of the polished section of copper concentrate



Legend:

a - General view of the polished section of copper concentrate;

b - Piece of the grain with bulk formation of copper sulfide on the surface of sulfur (zone I):

c -fragment of a grain with a crack in the mountains of sulfur that filled with copper sulfide,

d – fragment of a grain with a rim of copper sulfide on the surface of sulfur particles of.

1-cement (epoxy glue)

2-copper sulfides

3-sulphur

Elemental composition of the copper concentrate under study

by electron microscopy (grain 1 fragment I)

t-1

El.	Si	P	S	Ca	Ti	Cr	Mn	Fe	Ni	Cu	Zn	As	Cd	Sn	Sb	Bi	SUM
El.%	0,19	-	33,72	-	-	0,16	-	-	-	66,61	0,33	-	-	-	-	-	101

t-2

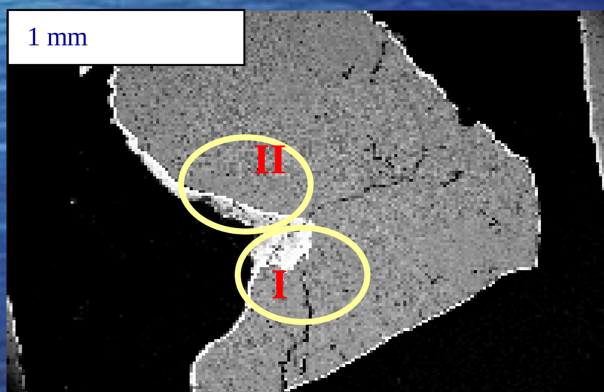
El.	Si	P	S	Ca	Ti	Cr	Mn	Fe	Ni	Cu	Zn	As	Cd	Sn	Sb	Bi	SUM
El.%	0,21	-	34,50	-	-	0,16	-	-	-	64,72	-	-	-	-	-	-	99,59

t-3

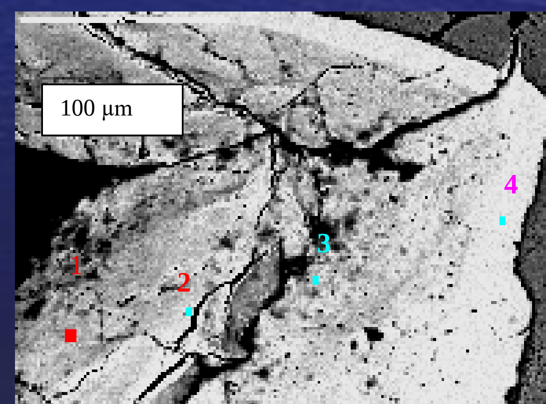
El.	Si	P	S	Ca	Ti	Cr	Mn	Fe	Ni	Cu	Zn	As	Cd	Sn	Sb	Bi	SUM
El.%	0,16	-	36,58	-	0,09	-	0,12	-	-	61,69	0,32	-	-	-	-	0,75	99,91

t-4

El.	Si	P	S	Ca	Ti	Cr	Mn	Fe	Ni	Cu	Zn	As	Cd	Sn	Sb	Bi	SUM
El.%	0,17	-	23,16	-	0,17	0,11	-	-	-	75,06	-	-	-	-	-	-	98,67



Grain fragment 1 of the analyzed sample
(increase x 35 times)



Fragment particles 1 zone I
(increase x 1000 times)

The rates of nodules processing

Product	Content, %						Recovery, %					
	Cu	Ni	Co	Mn	Mo	Zn	Cu	Ni	Co	Mn	Mo	Zn
Nodules	1,14	1,41	0,22	29,0	0,063	0,15						
Cu concentrate	59,40	0,02	0,003	0,03	-	0,02	88,31	0,002	0,02	0,002	-	0,23
Ni-Co concentrate	0,319	11,62	1,72	6,91	-	0,72	3,29	96,98	92,19	2,49	-	56,76
Mn concentrate	0,001	0,001	0,001	52,30	-	0,08	0,07	0,06	0,36	95,07	-	32,37
Cake	0,25	0,11	0,04	2,10	0,172	0,04	8,33	2,96	7,43	2,44	100	10,64

The advantages of the technology of polymetallic nodule leaching by sulfurous anhydride are the low energy consumption, accessibility of the required reagents, the possibility to carry out leaching at low temperatures and pressure and the efficient processing of the deep water ores of different chemical composition, including cobalt-bearing crusts with a high content of phosphorus.

THE CONTENT OF RARE METALS IN THE PRODUCTS OF NODULES PROSESSING

Product	Content, g/t													
	La	Sc	Sr	Y	Nb	Ce	Pr	Nd	Sm	Eu	Gd	Dy	Er	Yb
Nodules	83	9,25	577	66,2	18,8	294	29,9	113	35,3	7,99	27,1	27	16	14,9
Cu concentrate	12,3	1	3,31	0,21	0,32	35,9	0,6	18,6	6,56	1,78	4,89	5,2	1,3	2,23
Ni-Co concentrate	31,8	14	33,6	183	7,34	157	20	154	85,7	23,7	72,3	119	113	90,5
Mn concentrate	38,1	1	9,13	60,9	0,1	173	19	36,9	17,8	4,42	11,1	11	6,4	6,48
Cake	157	11,9	1398	20,2	30,6	367	21	78,7	18,4	4,11	11,2	8,2	5	4,31

DISTRIBUTION OF RARE METALS IN THE PRODUCTS OF NODULES PROCESSING

Product	Distribution, %													
	La	Sc	Sr	Y	Nb	Ce	Pr	Nd	Sm	Eu	Gd	Dy	Er	Yb
Nodules	100	100	100	100	100	100	100	100	100	100	100	100	100	100
Cu concentrate	0,25	0,18	0,01	0,01	0,03	0,21	0,03	0,28	0,31	0,38	0,31	0,33	0,14	0,25
Ni-Co concentrate	4,51	17,8	0,69	32,5	4,6	6,28	7,67	16,0	28,6	34,9	31,4	51,9	85,8	71,5
Mn concentrate	24,9	5,85	0,86	49,8	0,29	31,9	35,6	18,8	29,0	30	23,5	22,5	22,3	23,6
Cake	71,9	48,7	92,1	11,6	61,8	47,4	27,3	26,5	19,8	19,5	15,7	11,5	12,3	11

Hydrometallurgical sulfuric technology

Indicators of molybdenum leaching with solutions Na_2CO_3 and H_2SO_4

Na_2CO_3 leaching				H_2SO_4 leaching			
Concentration Na_2CO_3, %	Consumption Na_2CO_3, kg/t cake	Output cake, %	Molibdenum recovery %	Concentration H_2SO_4, %	Consumption H_2SO_4, kg/t cake	Output cake, %	Molibdenum recovery %
10	197	90,9	56,7	14	149	62,8	59,8
15	282	92,3	59,2	22	216	59,1	75,6
20	355	90,5	65,8	39	432	50,7	98,1

Metallurgical processing concept

Our concept for the metallurgical processing of raw ore material allows for the realization of one of two possible and fundamentally different technologies:

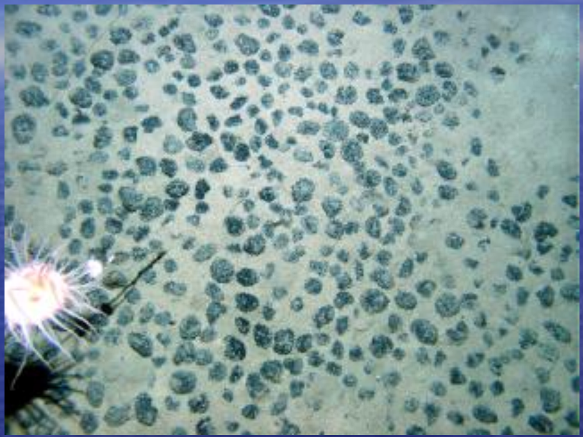
pyrometallurgical and hydrometallurgical.

Development of both technologies passed the stages of R&D and laboratory tests.

Separate units of technological schemes are checked in the enlarged laboratory and semi-industrial conditions.

The content of the useful components of the nodules and crusts

Names of elements	Contents, %	
	PMN	CFC
Cu	1,14	0,12
Ni	1,41	0,44
Co	0,22	0,64
Mn	29,0	22,3
Fe	5,24	16,6
Zn	0,15	0,06
Mo	0,063	0,04
SiO_2	11,98	9,0
Al_2O_3	4,19	5,3
CaO	2,23	5,4
MgO	3,06	2,4
TiO_2	0,52	1,4
P_2O_5	0,31	1,5
K_2O	1,20	0,7
Na_2O	2,19	2,4
C_{org}	< 0,1	-
S_{gen}	0,08	0,3
S_{sulf}	0,08	-
As	< 0,01	-
Sb	< 0,01	-
Au, g/t	< 0,01	0,06
Ag, g/t	< 0,05	2,07
Pt, g/t	-	0,4



Nodules in natural occurrence

Crusts in natural occurrence

The rates of crusts processing

Products	Output	Content, %					Share, %				
	%	Cu	Ni	Co	Mn	Fe	Cu	Ni	Co	Mn	Fe
Consumption											
Original crust	100	0,12	0,44	0,64	22,3	16,6	100	100	100	93,05	99,8
Electrolytic Mn	1,78				93,68	1,86				6,95	0,2
Total	101,78						100	100	100	100	100
Recovery											
Ni-Co concentrate	4,75	0,61	**8,45**	**12,62**	11,8	1,50	23,22	**87,72**	**90,06**	2,25	0,41
Mn concentrate	39,2	0,01	0,03	0,06	**59,00**	0,20	3,15	2,57	2,95	**92,91**	0,45
Cake	65,69	0,14	0,07	0,07	1,85	26,25	73,63	9,71	6,99	4,84	99,14
Total	109,26						100	100	100	100	100

Seafloor Massive Sulfides

Results of copper ore enrichment

Sample Ore type	Products	Output %	Content, %					Recovery, %				
			Cu	Zn	Fe	Au, g/t	Ag, g/t	Cu	Zn	Fe	Au	Ag
Sulfur	Copper concentrate	56,5	28,0	2,0	31,05	3,10	26,0	93,43	85,13	49,67	70,3	69,4
	Pyrite concentrate	43,5	2,56	0,47	40,90	1,70	14,9	6,57	14,87	50,33	29,7	30,6
	Ore	100,0	16,94	1,37	35,33	2,49	21,17	100,0	100,0	100,0	100,0	100,0
Inclusion	Copper concentrate	18,9	13,0	н/а	38,09	0,55	н/а	89,15	–	61,69	69,3	–
	Pyrite concentrate	9,4	2,0	–	21,50	0,10	–	4,48	–	16,44	6,0	–
	Mine tailing	70,7	0,1	–	3,8	0,05	–	4,37	–	21,87	24,7	–
	Ore	100,0	2,9	0,053	12,29	0,15	0,90	100,0	100,0	100,0	100,0	100,0

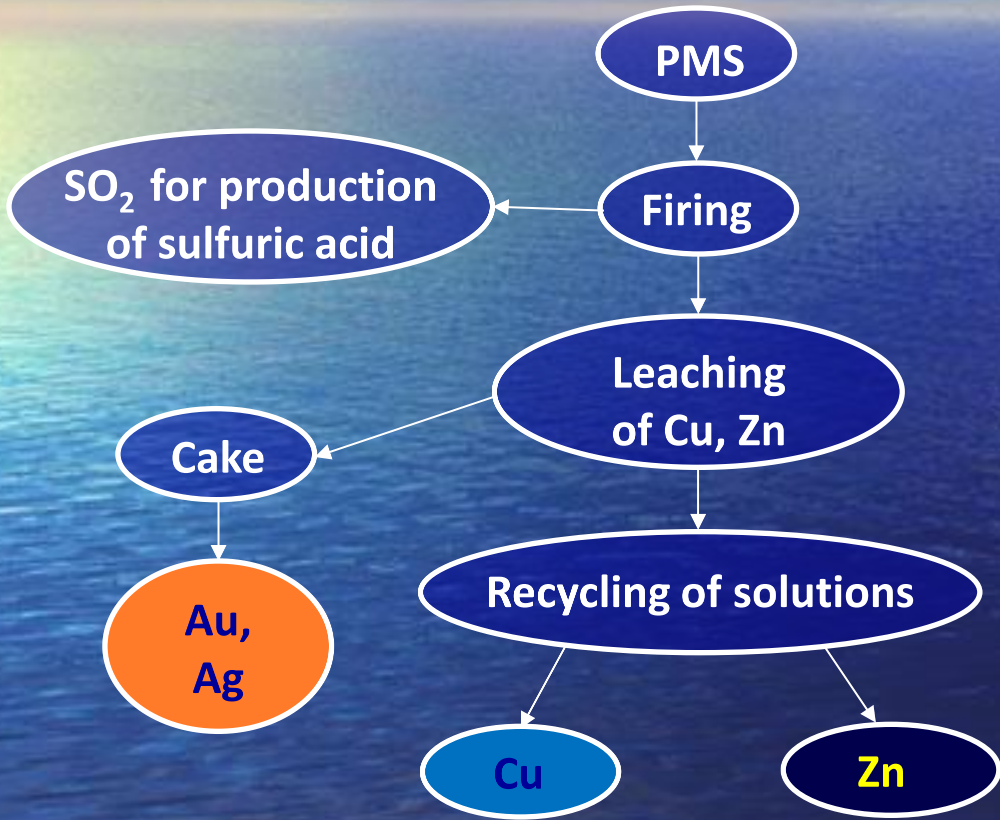
Results of zinc ore enrichment

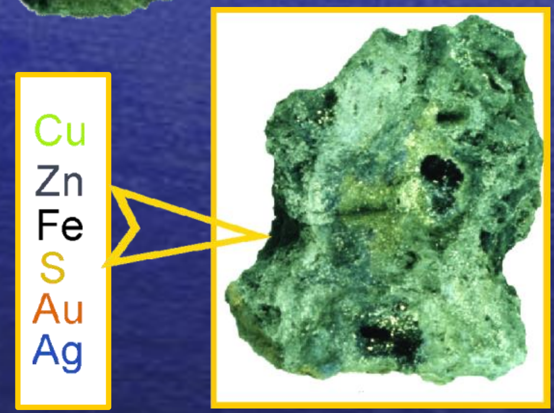
Sample Ore type	Products	Output, %	Content, %					Recovery, %				
			Cu	Zn	Fe	Au, g/t	Ag, g/t	Cu	Zn	Fe	Au	Ag
Sulfur	Zinc concentrate	36,79	0,55	51,05	11,50	11,89	251,13	75,43	97,13	12,92	83,39	89,25
	Pyrite concentrate	64,21	0,10	0,84	43,20	1,32	16,87	24,57	2,87	87,08	16,61	10,75
	Ore	100,0	0,26	18,81	31,85	5,10	100,71	100,0	100,0	100,0	100,0	100,0

Results of copper-zinc ore enrichment

Sample Ore type	Product	Output, %	Content, %					Recovery, %				
			Cu	Zn	Fe	Au, g/t	Ag, g/t	Cu	Zn	Fe	Au	Ag
Inclusion	Bulk concentrate	69,39	2,75	3,85	не ан.	не ан.	45,48	94,41	97,76	–	–	78,90
	Mine tailing	30,61	0,30	0,2	–	–	21,2	5,59	2,24	–	–	21,10
	Ore	100,0	2,0	3,45	12,3	0,18	40,0	100,0	100,0	100,0	100,0	100,0
Inclusion	Bulk concentrate	62,17	1,81	2,16	33,62	не ан.	не ан.	90,84	93,41	97,62	–	–
	Mine tailing	37,83	0,30	0,26	1,34	–	–	9,16	6,59	2,38	–	–
	Ore	100,0	1,21	1,68	21,41	0,1	6,7	100,0	100,0	100,0	100,0	100,0
Sulfur	Copper-zinc concentrate	20,26	23,95	15,48	26,08	5,49	27,0	92,44	90,90	20,24	32,32	82,16
	Pyrite product	79,74	1,12	0,39	31,20	2,92	14,9	7,56	9,10	79,76	67,68	17,84
	Ore	100,0	5,25	3,45	30,16	3,44	66,6	100,0	100,0	100,0	100,0	100,0
Sulfur	Copper-zinc concentrate	36,57	12,54	10,62	29,86	7,2	142,0	91,72	90,32	33,59	55,71	68,57
	Pyrite product	63,43	0,65	0,81	34,04	2,64	26,0	8,28	9,68	66,41	44,29	31,43
	Ore	100,0	5,00	4,30	32,51	3,12	62,0	100,0	100,0	100,0	100,0	100,0

Schematic diagram of hydrometallurgical sulfides processing





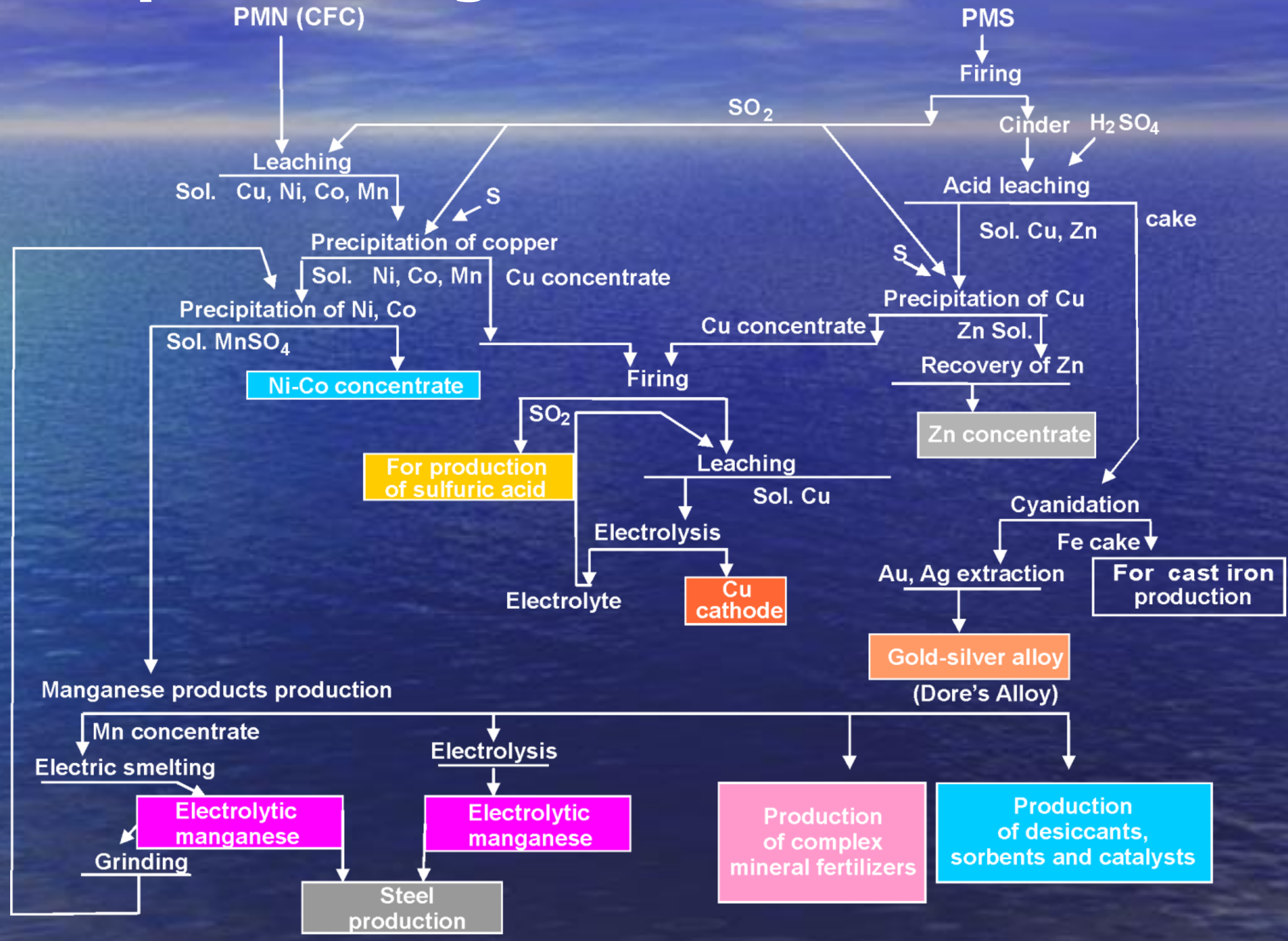
The technology is based on selective leaching of sulfides after firing followed by extraction of copper and zinc from solution. Also selenium and cadmium are recovered.

Rates of processing of one of the sulfide samples by combined technology

Products	Content, kg/m3, g/t, %						Recovery %					
	Cu,%	Zn,%	Co,%	Fe,%	Au, g/t	Ag, g/t	Cu	Zn	Co	Fe	Au	Ag
Consumption:												
PMS	13,07	7,67	0,33	27,7	5,6	53,41	100	40,01	100	100	100	100
Metallic zinc		85						59,99		0		
Recovery:												
Jarosite cake	1,94	0,44	0,012	29,99			1,554	0,601	0,379	11,319		
Cu concentrate	85,0	5,13	0,1	0,24		12,857	97,20	3,588	4,514	0,129		3,40
Zn concentrate	0,01552	40,496	0,67574	2,350			0,054	95,192	92,80	3,854		
Gold and Silver (with resin used)											96,42	88,46
Cyanidation tails (Iron concentrate)	0,4	0,3	0,017	60,89	0,52	10,9	1,181	0,598	1,980	84,687	3,58	8,14
Waste solution	0,00096	0,00304	0,00188	0,005			0,004	0,021	0,319	0,010		
Total:							100,0	100,0	100,0	100,00		

Scheme of joint processing of sulfides and nodules

The joint processing of oxide and sulfide ores from the World ocean is promising, in which the gases of burning of polymetallic sulfides are sent to the leaching of the polymetallic nodules, which allows to simultaneously solve the problems of reducing the cost of ore processing and protecting the environment.



Thank you for your attention!