

TECHNOLOGIES FOR THE PROCESSING OF POLYMETALLIC NODULES FROM CLARION CLIPPERTON ZONE IN THE PACIFIC OCEAN

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ABSTRACT

Polymetallic nodules (PN) have been recognized as a potential source of base metals such as: Cu, Ni, Co and Mn. However, the leaching and other processing methods of PN is complex and difficult due to their amorphous structure and the presence of metals as oxide and hydroxide form.

In the present paper three technologies for the recovery of base metals: Ni, Co, Cu and Mn from manganese nodules from the Clarion Clipperton Fracture Zone (CCZ) of the Pacific Ocean are reviewed and discussed. They were developed by research teams of the Interoceanmetal Join Organization (IOM):

- Hydrometallurgical technology of selective dissolving of PN nodules using sulfur dioxide (TECHNOLOGY I);
- A combined Pyro-hydrometallurgical technology for processing PN including reduction of nonferrous metals with coke (ore-smelting into electric furnace with producing of polymetallic alloy Cu-Ni-Co-Fe-Mn and SiMn slag and hydrometallurgical selective dissolution of alloy with resulting in a tradable product, a sulphide copper concentrate (54.9 % Cu and 30.9 % S) and high degree (> 99 %) of Ni, Co, Fe and Mn extraction in a productive solution (TECHNOLOGY II);
- Hydrometallurgical technology for processing of PN into autoclave by pressure sulfuric acid leaching (PAL) using reducing agents – molasses and pyrite. (TECHNOLOGY III).

It was found that for the choice of the technology for scaling up from laboratory tests to possible pilot plant experiments it is necessary to compare not only the efficiency of the results but also to conduct the deep economic analysis taking into account the possibilities for performance, the actual prices of metals, environmental pollution and others factors.

Keywords: manganese nodules, Clarion Clipperton Zone, hydrometallurgy, pyro-hydrometallurgy, autoclave processing.

INTRODUCTION

It is well known that the development of human civilization is determined by the energy and mineral

resources of the Earth. Forecasting the market for demand and supply of minerals and metals is a complex task [1 - 5]. The last studies from Global Commodity Markets [6] showed that the increase in metal prices

and the rapidly developing economies of China, India, Russia and Brazil reinforce the interest in the resources of the ocean floor.

Manganese nodules, also known as polymetallic nodules, were discovered at the end of the 19th century in the Kara Sea, in the Arctic Ocean of Siberia (1868). During H.M.S. Challenger's (1872-76) scientific expeditions, they were found to occur in most oceans of the world. However, it was only following Mero (1965) publication *Mineral Resources of Sea* that the worldwide interest in seabed exploitation or deep-sea mining began [7].

At present, there is a sufficiently comprehensive data base on the Clarion Clipperton Zone (CCZ). This area is located in the eastern central Pacific, to the south and south-east of the Hawaiian Islands. This region is considered to be the best in terms of commercial interest for

manganese nodule recovery. It lies in international waters, and stretches approximately from 0°N - 23°30'N, and from 115°W - 160°W, an area of approximately 4.5×10⁶ km² (Fig. 1). Nine contractors have exploration contracts in the CCZ through the International Seabed Authority (ISA). The list of contractors includes China, Japan, South Korea, France, Interoceanmetal Joint Organization, Russian Federation, Germany, Tonga Offshore Mining, Nauru Ocean Resources, Belgium, Kiribati, Cook Islands Investment Corporation, Singapore, UK Seabed Resources. The Interoceanmetal Metal Organization (IOM) was formed on April 1987, based on the Intergovernmental Agreement. The present IOM states are: Bulgaria, Cuba, Czech Republic, Poland, Russian Federation and Slovakia. On 29 March 2001, the IOM signed with the International Seabed Authority (ISA) the contract for exploration for polymetallic nodules within a 75000 km² area situated

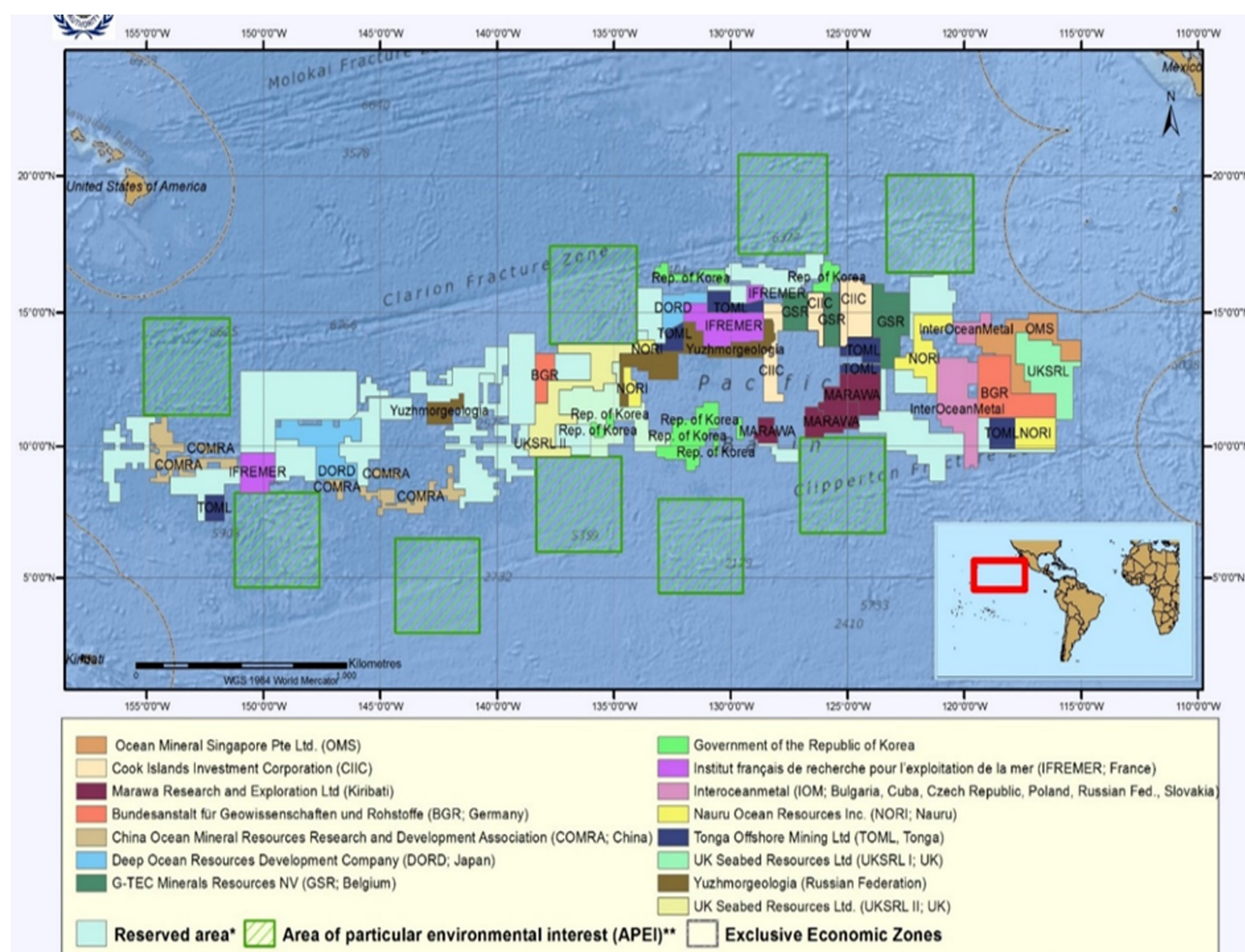


Fig. 1. Polymetallic nodules exploration areas in the Clairon Clipperton Fracture Zone Background map: ESRI, International Seabed Authority, 24 July 2014.

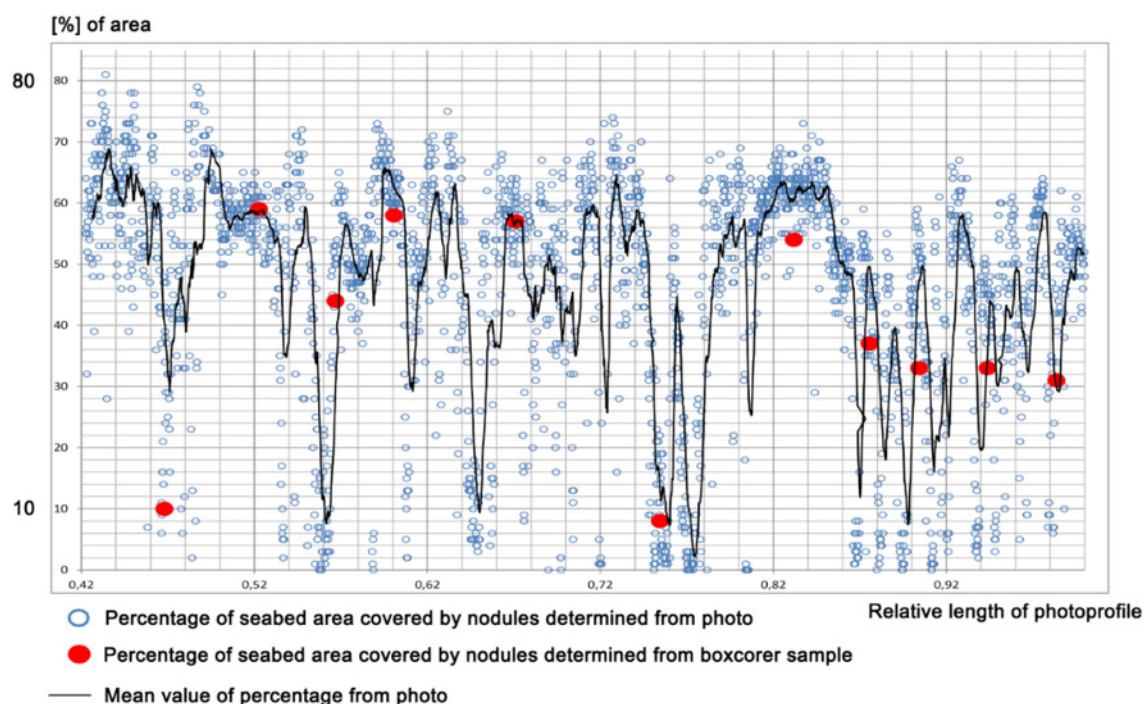


Fig. 2. Percentage of seabed area covered by nodules determined from photo, CCFZ – IOM.

in the CCZ.

IOM has been carrying out research works on polymetallic nodules for many years and at different phases the activities included: geological exploration, mining technology, processing technology and metallurgy and environmental research.

A coverage of seabed by nodules, one photo profile of length about 10 km is shown on Fig. 2.

Characteristics of polymetallic nodules from CCZ

Deep sea polymetallic nodules represent sedimentary formations that cover the bottom of the oceans and some seas (Fig. 3). The largest deposits of ores are registered in the Pacific Ocean between Hawaii, California and around Polynesia. Besides exploration contractors' work for polymetallic nodules a lot of other research has been carried out, e.g. in-depth analysis of the nodules in this region was made by LRET Group [7].

Deep-sea polymetallic nodules are considered as an

important unconventional resource for nickel, copper, manganese and cobalt. Except these metals they content a large variety of metals, including molybdenum, zinc, zirconium, lithium, platinum, titanium, germanium, yttrium and some REEs metals, which increased the nodules combined value as alternative supplies for expanding economies and emerging green energy technologies [8 - 10].

These metals are represented in the nodules as oxides and hydroxides and usually are integrated in the crystal lattice of manganese and iron oxides.

The major matrices for Mn and Fe are: todorokite ($\text{Mn}^{4+}, \text{Mn}^{2+}, \text{Mn}$) $_6\text{O}_{12} \cdot 3\text{H}_2\text{O}$, buserite ($\text{Na}_{14}\text{Mn}_{14}\text{O}_{27} \cdot 21\text{H}_2\text{O}$, birnessite (Na, Ca) $_{0.5}(\text{Mn}^{4+}, \text{Mn}^{3+})_2\text{O}_4 \cdot 1.5\text{H}_2\text{O}$), manganite - (Na, Ca_3) $\text{Mn}_{70}\text{O}_{140} \cdot 28\text{H}_2\text{O}$, vernadite - ($\text{Mn}^{4+}, \text{Fe}^{3+}, \text{Ca}, \text{Na}$)(O, OH) $_2 \cdot n\text{H}_2\text{O}$, goethite ($\text{FeO} \cdot \text{OH}$), magnetite (Fe_3O_4) or hematite (Fe_2O_3), where nickel and copper are mainly associated with manganese and cobalt mostly with the iron phase, but possibility with

Table 1. The average chemical composition of PN from CCZ.

Mn, %	Ni, %	Cu, %	Co, %	Fe, %	Zn, %	Mo, %
30.8	1.31	1.23	0.19	5.25	0.14	0.062
SiO ₂ , %	TiO ₂ , %	Al ₂ O ₃ , %	MgO, %	CaO, %	Na ₂ O, %	K ₂ O, %
13.10	0.4	4.24	3.37	2.31	3.12	1.15

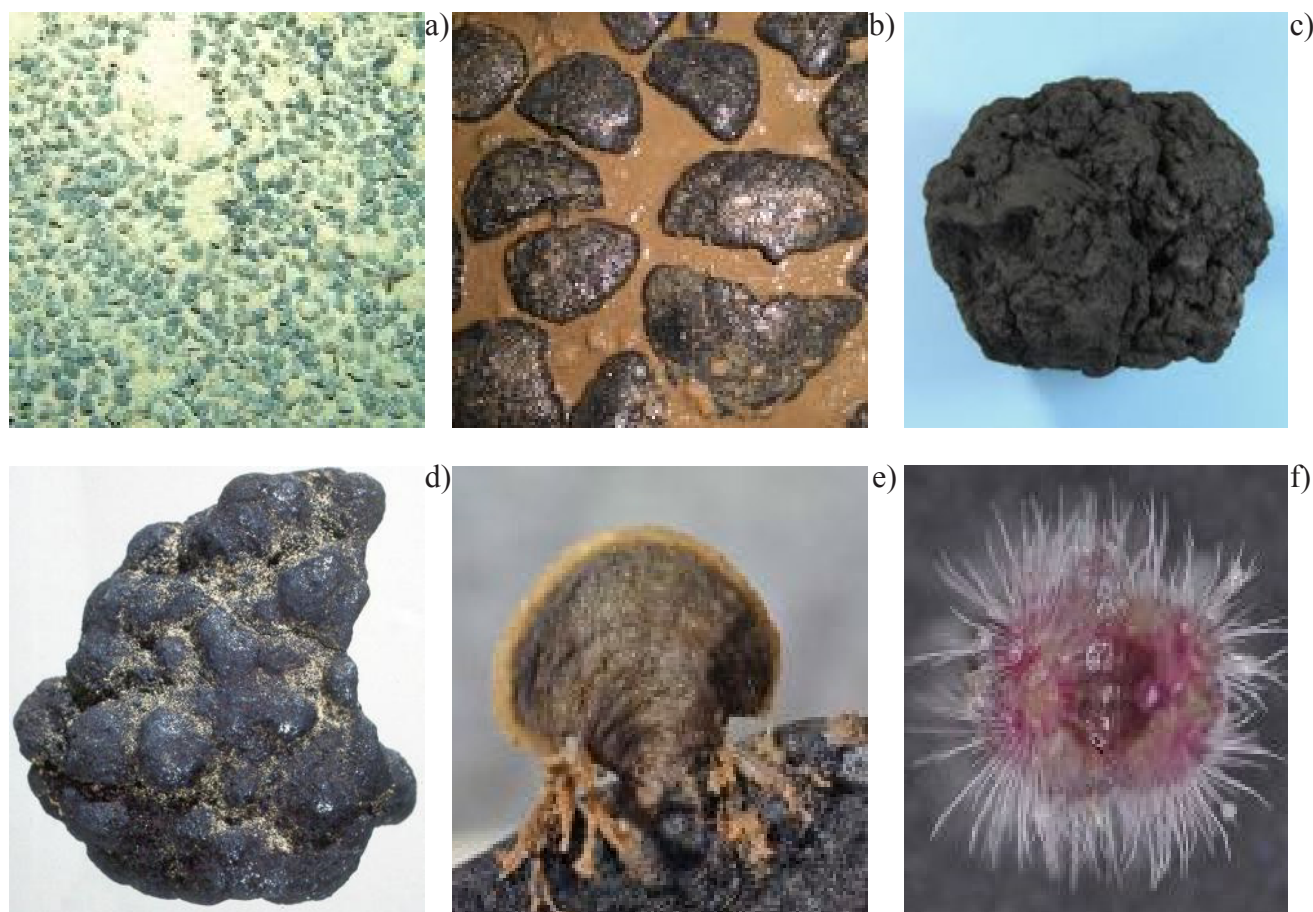


Fig. 3. Nodules on the ocean floor at 4000-5000 m depth (a,b), minerals todorokite and bernassite (c,d) and polymetallic nodules with specious of fauna (e, f).

the manganese oxides. The most stable species of these element in the ocean environment are MnO_2 , Fe_2O_3 , CuO , Ni_3O_4 and Co_2O_3 [7].

The average chemical composition of PN from Clarion Clipperton Zone is shown in Table 1.

In the mining process a dilution with bottom sediments nodules occurs. The chemical composition of sediments is in mass %: SiO_2 - 16.1; Ti - 0.35; CaCO_3 - 3.66; Fe - 4.4; C org. - 0.41; Ni, Cu, Co, Mn, Zn - less than 0.1 %. The sedimentation content is low, approximately around 8 -10 %.

A short review of technologies for PN processing

A variety approaches and technologies in the laboratory scale have been developed for the extraction of the valuable metals from polymetallic nodules. They can be divided into two groups: combined pyro-hydrometallurgical, hydrometallurgical and bio-hydrometallurgical.

During pyro-metallurgical pretreatment of manga-

nese nodules Cu, Ni, Co are concentrated in intermediate product - alloy [11 - 14]. Satyabrata et al. [15] propose oxidation of the alloy and sulphidation with elementary sulphur to matte. Another method for processing of the matte has been developed by Tetsuyoshi et al. [16]. The authors have carried out converting of the matte in order to complete the iron removal. The lower concentration of iron and manganese in the resulting solutions significantly alleviate further selective extraction of copper, nickel and cobalt from it.

The hydrometallurgical process for dissolving of alloy used sulphuric and sulphurous acids or ammoniacal as a medium for leaching [17, 18] .

In direct hydrometallurgy leaching in sulfuric acid various reductants were investigated including sulfur [19]; SO_2 or sulfuric acid [20 - 22]; glucose [23]; charcoal [24]; ferrous ion [25]; pyrothite [26]; molasses and pyrite [27]. Among these reductants, SO_2 and FeSO_4 are two of the effective reductants for MnO_2 leaching.

A polymetallic manganese nodules pilot plant of 500 kg per day processing capacity was designed and set up at Hindustan Zinc Limited, Udaipur (India) [28]. The process was based on the reductive alkaline pressure leaching of nodules using SO_2 as reducing agent in the presence of ammonia at pH 8 - 9.

Another option is the biohydrometallurgical process, even though it is commonly used for copper, gold and uranium recovery. The idea is to introduce organisms and/or microbes to process bioreduction of manganese dioxide [10].

The current state of development of technologies of IOM

In the period of 2001-2012 the InterOceanmetal Joint Organization carried out extensive research on the improvement and optimization of the basic technological process for recovery of the base metals: Cu, Ni, Co and Mn from polymetallic manganese nodules (PMN). IOM has developed three technologies on the lab-scale, based on the existing facilities in the organization member countries:

- Hydrometallurgical technology of selective leaching of metals from polymetallic nodules using sulfur dioxide (TECHNOLOGY I). This technology has been developed in TSNIGRI Institute in Russia [20].
- A Combined Pyro-hydrometallurgical technology, has developed in CNIChermet, Russia and the University of Chemical Technology and Metallurgy, Bulgaria. The pyro-metallurgical route, includes selective electro-reduction of nonferrous metals (Ore-Electric Smelting Furnace) with producing of polymetallic FeCuNiCoMn alloy and SiMn slag and subsequent treatment of complex alloy - hydrometallurgical route, (TECHNOLOGY II) [16];
- Hydrometallurgical technology for processing of PN in autoclave by pressure sulfuric acid leaching (PAL) using reducing agents - molasses and pyrite, (TECHNOLOGY III). It has developed in CEDINIQ -CIPIMM in Moa Republica de Cuba [26].

Hydrometallurgy PN processing with reducer SO_2 , TECHNOLOGY I

The scheme of hydrometallurgical PN processing is shown in Fig. 4.

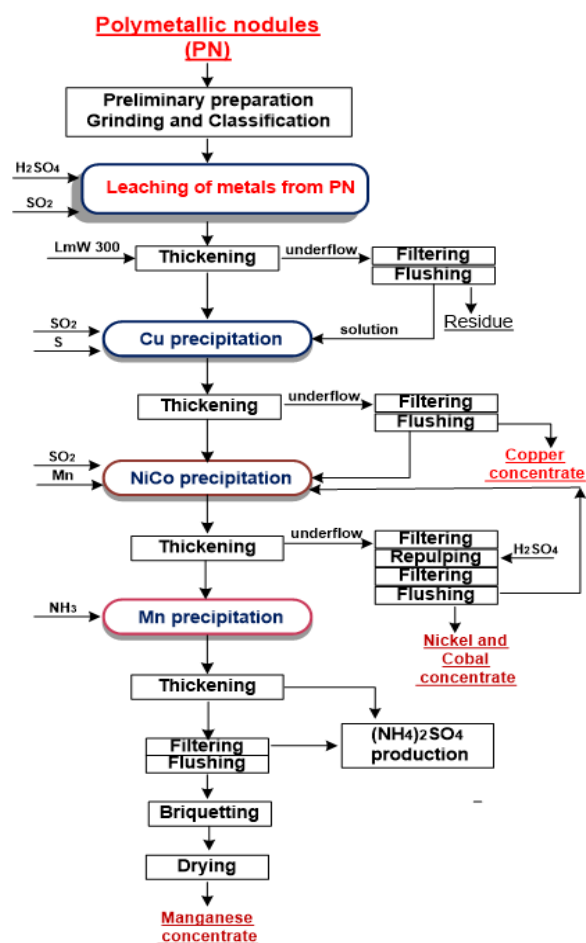
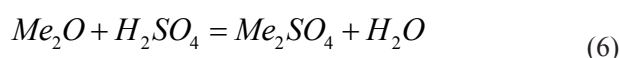
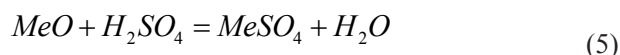
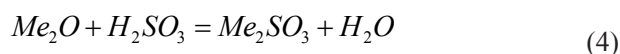
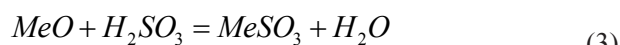
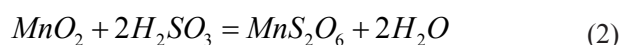


Fig. 4. Simplified flow sheet of hydrometallurgical PN processing with the use SO_2 (TECHNOLOGY I).

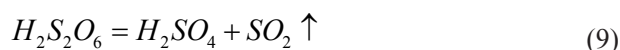
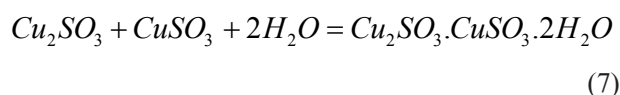
The technology consists of the following operations:

- Preliminary grinding of wet raw material in ball mills up to 86 % - particle size 0.2 mm;
- Selective leaching of copper, nickel, cobalt and manganese dioxide at atmospheric pressure containing SO_2 , thickening of the pulp after PN leaching with the use of flocculants, and filtering of the bottom discharge thickener;
- Selective precipitating of the copper from solution through introduction of activated sulphur powder and feeding of sulphuric anhydride into the reactor at atmospheric pressure;
- Precipitation of nickel and cobalt concentrate by introduction of powdered sulphur and metallic manganese;
- Precipitation of MnO_2 in the solution's neutralization reaction with ammonia water, thickening, filtering, washing the filter with manganese hydroxide concentrate, drying in rotating furnace and briquetting.

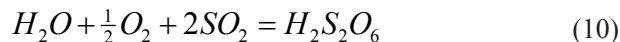
The base chemical reactions during leaching in the presence of aqueous SO_2 are as followed:



where Me is Cu, Ni, Co, Fe, Ca, Mg.



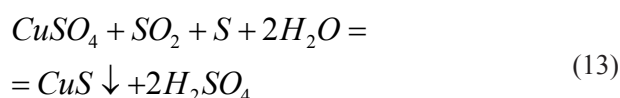
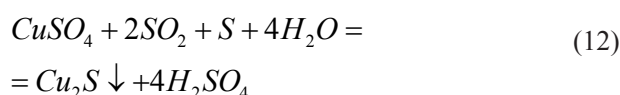
In the presence of dissolution oxygen are possible other reactions



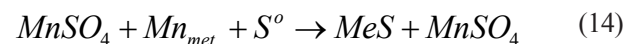
The leaching process takes place at 343 - 353K temperature and atmospheric pressure. The gases released during burning of sulphur or roasting of pyrite concentrates can also be used for extraction of the useful components from nodules (SO_2 10 - 16 %).

Selective precipitating of the copper from solution was carried out through introduction of activated sulphur powder and feeding of sulphuric anhydride into the reactor at atmospheric pressure. Under these circumstances, a high degree of copper sulphide precipitation was achieved.

The chemical reactions during selective precipitation with activated sulphur powder and SO_2 are as followed:



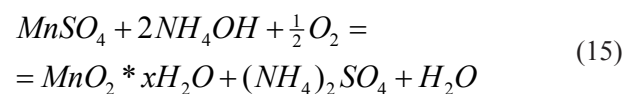
The chemical reactions during Ni-Co concentrate precipitation with powdered sulphur and metallic manganese are followed:



where Me is Ni and Co.

The manganese contained in the Ni-Co concentrate is dissolved through its repulping in sulphuric acid solution. Thus, the whole quantity of metallic manganese passes into the solution with subsequent regeneration.

Precipitation of MnO_2 in the solution's neutralization reaction with ammonia water, thickening, filtrating, washing the filter with manganese hydroxide concentrate, drying in rotating furnace and briquetting. Chemical reactions during manganese concentrate precipitation are:



As a result of nodules processing by the sulphuric acid method with reducer sulphuric oxide, commercial products with the following chemical composition are obtained: copper concentrate with copper contents about 40 %; Ni-Co concentrate contains 20.8 % Ni and 2.7 % Co and Mn concentrate with 62 % Mn. The recovery of metals from the concentrates are: 92 % Cu, 96 % Ni, 92 % Co and 96 % Mn.

A combined pyro-hydrometallurgy technology for PN processing. TECHNOLOGY II

The technology consists of two routes: pyro- and hydrometallurgical. Pyrometallurgical route includes selective reduction of non-ferrous metals to a complex polymetallic FeCuNiCoMn alloy and transition of the manganese and ferrous oxides to the slag phase with its subsequent processing to obtain silicomanganese alloys. The process of reduction was carried out after drying of PN with composition in mass %: 24.0 Mn, 5.75 Fe, 1.11 Ni, 1.04 Cu and 0.12 Co from CCFZ of the Pacific Ocean at a temperature of 723 K and reduction smelting at 1723 - 1773 K in the presence of coke. The chemical composition of polymetallic alloy (PMA) was as allowed in mass %: 12.07 Cu, 12.81 Ni, 1.33 Co, 65.9 Fe, 5.33 Mn, 1.07 C, 0.97 P and 0.54 others. The high-manganese slag subject to processing contains in mass %: 47 Mn, 1.07 Fe and 0.04 P.

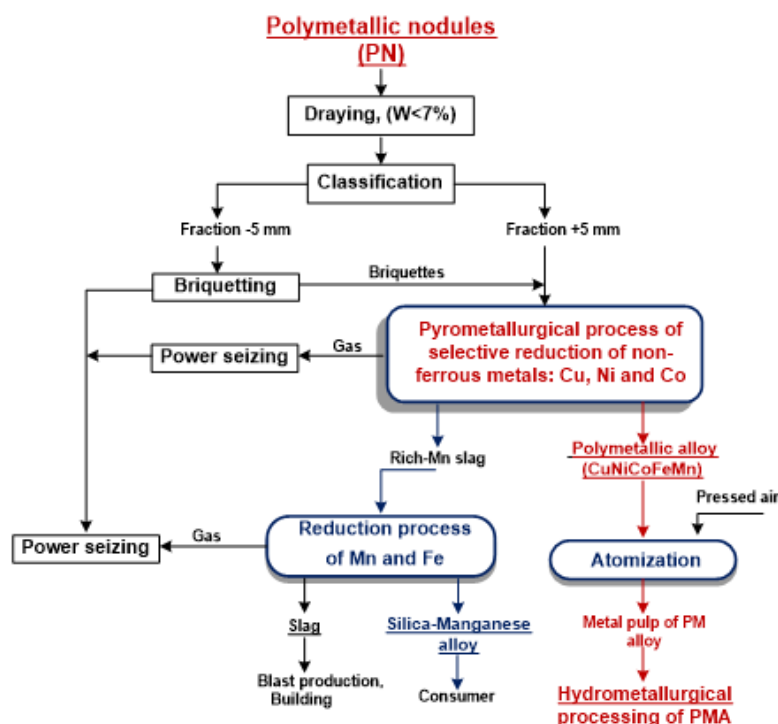


Fig. 5. Simplified flow sheet of pyrometallurgical route of combined pyro-hydrometallurgical PN processing (TECHNOLOGY II).

A schematic flow sheet for pyrometallurgical PN processing is shown on Fig. 5.

The developed hydrometallurgical scheme for processing consists of the following technological processes: i) two stage dissolution of alloy into sulfuric acid solution in the presence of sulfur dioxide with copper reporting to leach residue; ii) autoclave dissolution of copper sulphide residue; iii) sulphide precipitation of nickel and cobalt from leach liquor, iv) hydrolysis and manganese; v) autoclave dissolution of copper and nickel sulphide precipitates; vi) separation of cobalt from nickel by solvent extraction with Cyanex 272 extractant and re-extraction with cobalt electrolyte. The obtained Cu, Ni and Co electrolytes have composition suitable for the extraction of copper electrowinning.

A schematic flow sheet for hydrometallurgical treatment of PA with metallic copper, nickel and cobalt recovery is shown on Fig. 6.

Two stage selective dissolution of alloy into sulfuric and sulphurous acids includes reductive dissolution of the alloy in sulfuric acid in the presence of sulfur dioxide in the first stage and oxidation in the presence of dissolved air in the second stage.

The optimal parameters of this process are detailed

description in [13]. Indisputable advantage of the method is the selective dissolution of the alloy at which over 99 % of the copper concentrate into insoluble residue in the form of copper sulfides (CuS , Cu_7S_4). The content of copper in the residue reaches 54.9 %, and it can be classified as a rich sulphide copper concentrate and represents a commercial product. The degree of the other metals extraction into the solution is as follows in mass %: 98.3 Fe; 99.2 Mn; 94 Ni and 94.3 Co.

The process of Ni-Co sulfide sludge precipitation was conducted at equilibrium pH = 3.6, 150 % excess of NH_4HS than stoichiometrically required and temperature 303 K. Neutralization of the solution was made with 32 % w/v solution of lime. The chemical compositions of the obtained Ni-Co concentrate contains: 30.3 % Ni and 3.13 % Co. Further, the mixed Ni-Co sulphide sludge is treated in an autoclave by an oxidation dissolution, and the solution undergoes to hydrolysis purification from iron and manganese.

The most effective purification of the solution from iron was achieved in an autoclave. The obtained jarosite precipitation was large crystalline and well filtered. A purification from manganese and the residual heavy metals content was carried out by neutralization with

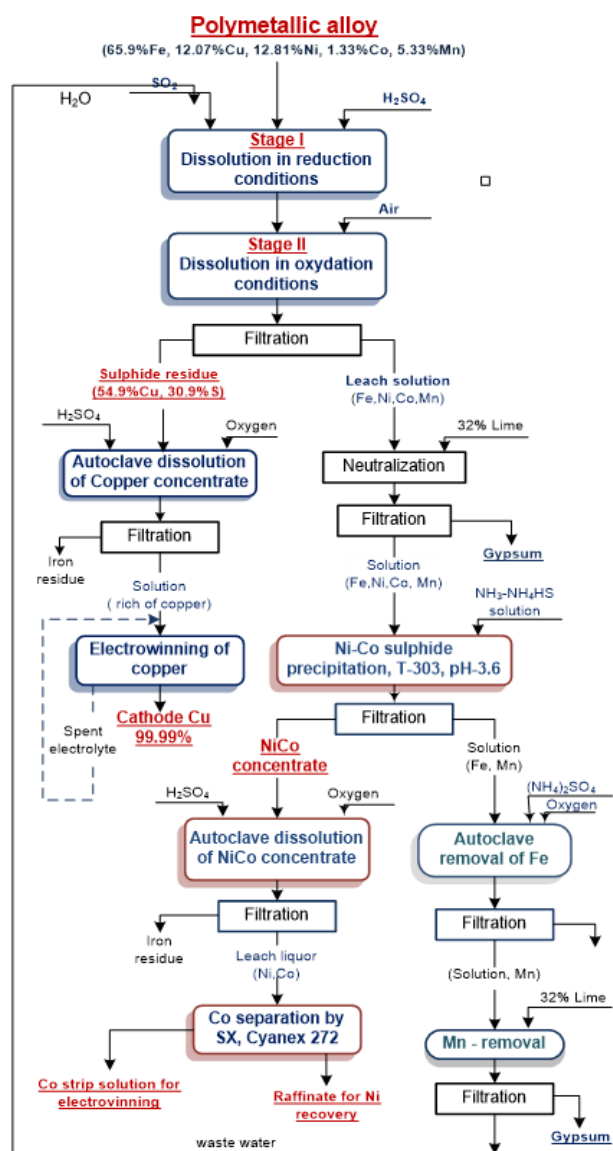


Fig. 6. Simplified flow sheet of hydrometallurgical route of combined pyro-hydrometallurgical PN processing (TECHNOLOGY II).

32 % w/v solution of lime.

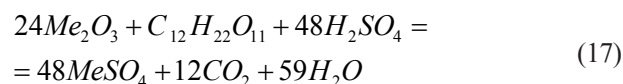
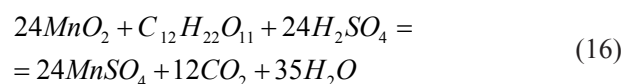
Autoclave method was proposed for leaching of copper from the sulphide residue with simultaneous purification of the solution from iron. The resulting solution had a composition suitable for the recovery of copper through electrolysis.

The process of extraction of nickel and cobalt from Ni-Co sulphide precipitations passes through the following operations: autoclave dissolution and separation of cobalt from nickel by solvent extraction with Cyanex 272 extractant and re-extraction with spent cobalt electrolyte [29].

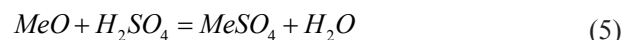
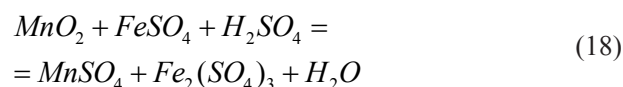
Pressure hydrometallurgical technology with molasses and pyrite. TECHNOLOGY III

Hydrometallurgical technology for processing of PN in autoclave by pressure sulfuric acid leaching (PAL) using reducing agents - molasses and pyrite, includes the following main operation: i) direct preparation of PN pulp with high solids concentration; ii) pressure acid leaching using reducing agents - molasses and pyrite; iii) direct extraction and separation metals by RIP process; iv) copper sulfide precipitation; v) solvent extraction of Zn; vi) precipitation of nickel and cobalt sulfides; vii) obtaining of manganese oxide by calcination. The flow sheet of hydrometallurgical pressure leaching (PAL process) is shown on Fig. 7.

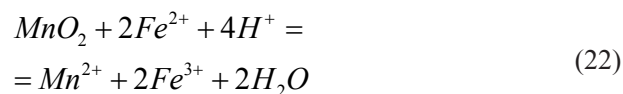
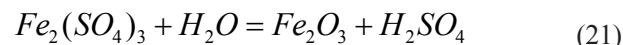
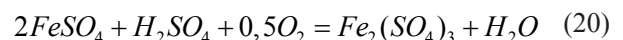
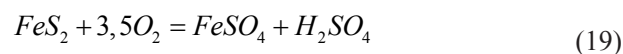
Principal reactions that occur in the leaching process in the presence of molasses and pyrite are:



where Me are Co, Fe.



where Me are Cu, Ni, Co, Zn, Al.
With pyrite



According to M. Pelegrin Rodriguez et al. [27] the optimal parameters of leaching process with molasses were as follows: temperature 413 K, solid inside the autoclave 31 %, duration 60 minutes, acid/PN 0.8 kg/kg and molasses/PN - 0.12 kg/kg. In these conditions, a

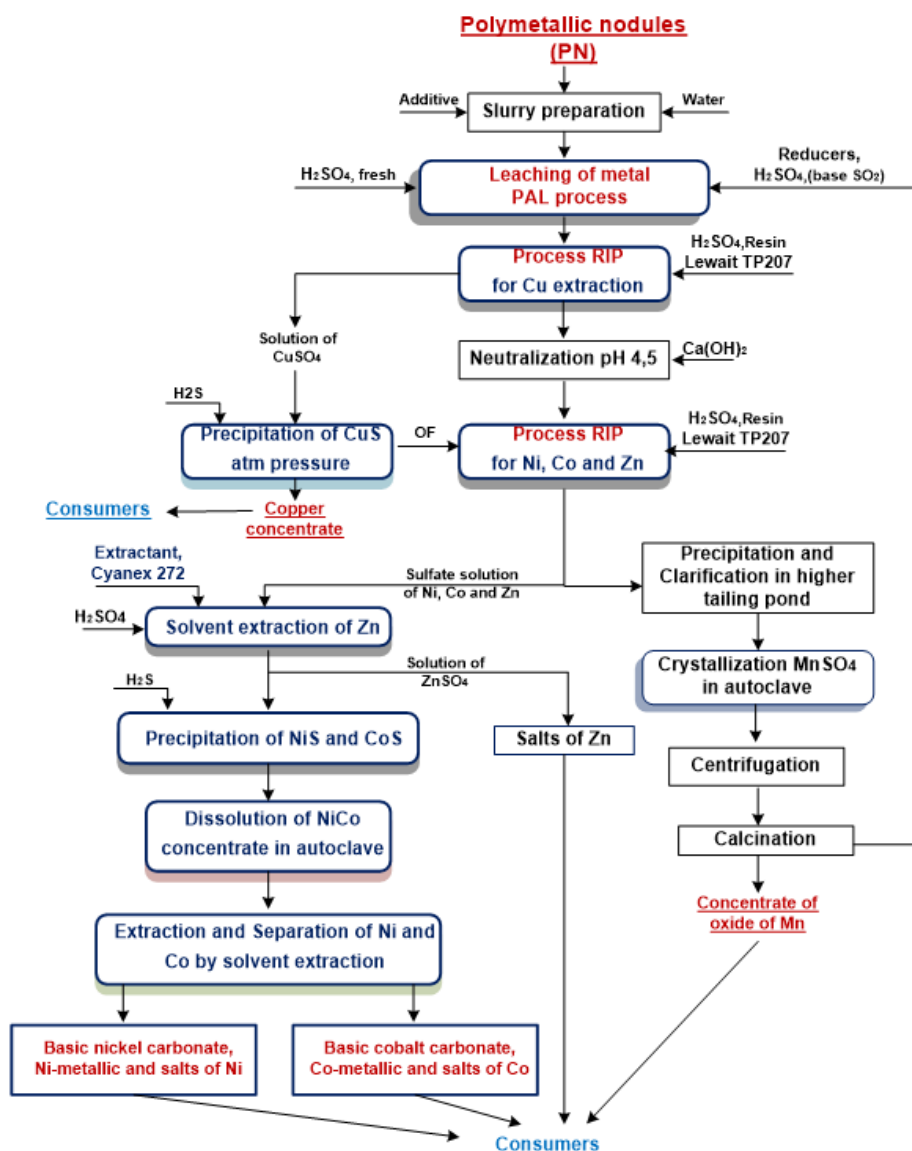


Fig. 7. Simplified flow sheet of hydrometallurgical pressure PN processing with the use of molasses and pyrite.

high degree of extraction of useful metals, except Fe, has been achieved (%): Ni - 97.70; Cu - 91.77; Co - 98.31; Mn - 97.07; Fe - 24.54; Zn - 97.07.

For extraction and separation of non-ferrous metals from liquor was used ion exchange method - RIP (resin-in-pulp) process. The process using resin is Lewaitit TP 207. It consists of two steps: RIP process for copper and RIP process for nickel, cobalt and zinc.

The precipitation of copper, nickel and cobalt was carried out with H_2S . The process of solvent extraction of Zn was carried out with Cyanex 272 at $pH = 2$. For the re-extraction process was used sulphuric acid. Thus, from a zinc sulphate solution we can obtain vari-

ous compounds of this metal, depending on the market requirements.

Precipitation of nickel and cobalt sulfides was realized in an autoclave. For this purpose, the solution was neutralized with limestone to $pH = 2$. Deposition was realized during 25 minutes at the temperature of 394 K and the total pressure inside the autoclave was 10 bar (partial pressure of $H_2S \sim 9$ atm).

The recovery of Mn from solution includes: preliminary heating to temperature about 353 K, and precipitation in the autoclave at the temperature 433 - 463 K of crystals $MnSO_4 \cdot H_2O$. Furthermore the crystals are sent to the calcining furnace, where they are calcined to

Table 2. Annual production of metal content for three technologies.

Products (Metals content)	TECHNOLOGY I	TECHNOLOGY II	TECHNOLOGY III
Cu concentrate, (Cu)	34 024	28 517	34 876
Ni Co concentrate, (Ni)	30 656	28 542	29 106
Ni Co concentrate, (Co)	4 450	3 874	4 770
MnO ₂ · xH ₂ O, Mn	860 430	-	585 130
SiMn alloy		561 522	-
(NH ₄) ₂ SO ₄	2 071 211-	-	-
ZnSO ₄	-	-	9 667

obtain manganese oxide. Depending on market conditions one can produce MnO, MnO₂, or other oxides of commercial interest.

Analysis of technological schemes

Comparative analysis of the three technologies shows that the major differences consist in the methods used for extraction and concentration of valuable metals (Cu, Ni, Co, Mn): selective leaching of copper, nickel, cobalt and manganese dioxide at atmospheric pressure containing SO₂ (Technology I), a high temperature reduction of non-ferrous metals and concentration of non-ferrous metals in polymetallic alloy and two stage selective dissolution of alloy into sulfuric and sulphurous acids (Technology II) or pressure acid leaching using reducing agents - molasses and pyrite and concentration of the metals by use of ion exchange resins (Technology III).

The same methods were used for the extraction of the metals from liquors: sulphide precipitation of Cu, Ni and Co and dissolution of the obtained sulphide sludge in autoclave. For the separation of nickel from cobalt the method of solvent extraction with extractant Cyanex 272 was used. The resulting solutions were subjected to electrolysis or to precipitation of salts.

In Table 2 are given the preliminary products obtained from the three technologies and annual quantities of content metal estimated on the base pre-feasibility study during PN processing, approximately 3 million tons per year. The full metals recovery in product is given in Table 3.

The lower degree of metals extraction following Technology II are due to a significant losses of valuable metals in the slag melt during smelting in the electric furnace. For increasing of these parameters is necessary to use more advanced processes such as smelting in liquid bath or plasma process.

CONCLUSIONS

The lively interest in polymetallic manganese nodules during 80's continues today. The liberal market and globalization will determine the time limits and rates of utilization of the unique deposit of metals, regardless of the depth at which they are located. The deep sea mining community anticipates that pilot mining test or mining collectors tests will be carried soon and provide the data for economic assessment and environmental impact analysis. Although the IOM has the significant experi-

Table 3. Full metals recovery in product, %.

Metal	Technology I	Technology II	Technology III
Cu	92.06	89.90	87.10
Ni	96.14	83.42	93.20
Co	92.54	84.20	94.10
Mn	95.51	72.58	96.60
Zn	-	-	93.50

ence in the extractive metallurgy polymetallic nodules we consider that for further advances is necessary to conduct experiments at larger scale. Only then we will be able to make the right choice on the most suitable technology for extraction of valuable metals from PN and to optimize the process for costs and sustainability.

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