*Chemistry for Sustainable Development* **19** (2011) 383–387

UDC 622.765+634.0.864

# Modified Lignins as Depressor Reagents for Flotation of Disseminated Copper-Nickel Ores

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(Received October 28, 2010; revised March 14, 2011)

## Abstract

Results are presented concerning studying the use of modified kraft lignin (sulphate) as a depressor reagent for non-metallic minerals in the flotation of disseminated copper-nickel ores. It was found that the modification of lignin according the Mannich reaction (aminomethylation) is a convenient method to implement and technologically sound recycling of the high-tonnage waste of pulp and paper industry.

**Key words:** flotation, disseminated ores, depressors, modification of kraft lignin, aminomethylation

## INTRODUCTION

Recent data concerning the structure of the resources of commercial type sulphide copper-nickel ores from the Norilsk deposits indicate that the fraction of disseminated ore is equal to 84 %, that for rich ore being of 9 %, whereas that for cupriferous ore is equal to 7 % [1]. In the future, the proportion of disseminated ores in the total processing of industrial type Norilsk copper-nickel ores will increase.

The disseminated ores of the Norilsk copper-nickel deposits are considered a promising source of platinum-metal raw. The disseminated ores of the Norilsk deposits involved in the mining and processing are superior in the concentration of platinum group metals (PGM) with respect to all copper-nickel and almost all PGM deposits of the world. Their processing is focused on the most complete extraction of both non-ferrous and precious metals.

The main ore-forming minerals disseminated ores comprise pyrrhotite, chalcopyrite, cubanite, pentlandite, as minor minerals pyrite, mackinawite, violarite, sphalerite, galena, nickeline, argentopentlandite, wallerite, and marcasite. Oxide minerals are presented by magnetite, titanomagnetite, ilmenite, chrome spinel, occasionally hematite. Rare formations are presented by precious metal minerals. Platinum, palladium, rhodium, gold and silver in sulphide ores occur in two forms: forming proper minerals or being isomorphically included as a part of the main ore-forming minerals.

The main gangue minerals are presented by feldspar, pyroxene, olivine, and the secondary ones being presented by serpentine, talc, chlorite, actinolite, hornblende, and mica [2].

The quantitative mineralogical analysis data concerning the disseminated ores (Table 1) indicate a high content of rock-forming minerals many of those represent flotoactive species to pass into concentrates, which significantly reduces the quality of the latter.

The concentrates obtained *via* enriching the disseminated ores are characterized by a low content of valuable components being to a considerable extent diluted by refractory gangue minerals.

In this regard, one of the most urgent problems that arise in the course of processing these ores consists in searching and using gangue depressors in their flotation.

TABLE 1

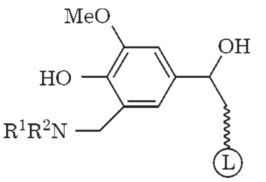
Results of quantitative mineralogical analysis of initial ore, with particle size 2–0 mm

| Size grade, mm | Content, % | | | | |
|---|---|---|---|---|---|
| | Pyrrhotite | Pentlandite | Chalcopyrite | Magnetite | Main rock-forming minerals* |
| −2 + 1 | 10 | 7 | 8 | 3 | 50 |
| −1 + 0.5 | 20 | 5 | 10 | 10 | 60 |
| −0.5 + 0.25 | 25 | 10 | 20 | 7 | 50 |
| −0.25 + 0.125 | 15 | 10 | 5 | 10 | 50 |
| −0.125 + 0.074 | 15 | 8 | 12 | 4 | 50 |
| −0.074 + 0.044 | 10 | 4 | 8 | 10 | 10 |
| −0.044 | 17 | 10 | 15 | 10 | 10 |

*Pyroxene, feldspar, olivine.

In order to suppress the flotation activity of silicate rocks one uses such depressors as carboxymethylcellulose (CMC), carbosulphite and carbothion sulphate, trisodium phosphate, dextrin, starch, sodium silicate, lignosulphonates *etc.* [3, 4].

We investigated the possibility of using modified kraft lignin **L-1**–**L-4**, a large-tonnage waste pulp and paper industry as a gangue depressor reagent in the flotation of disseminated ore from the Norilsk-1 deposit:



**L-1** $R^1 = R^2 = CH_3$ (hydrochloride)
**L-2** $R^1 = R^2 = CH_3$
**L-3** $R^1 = R^2 = CH_2CH_2OH$
**L-4** $R^1 = CH_3$; $R^2 = CH_2CH_2OH$

## EXPERIMENTAL

The depressor reagents under investigation were prepared by means of the method we developed [5] based on the reaction of secondary amines and formaldehyde with sulphate lignin dissolved in black liquor. The elimination of the stage of lignin isolation from the liquor simplifies the process of modifying this substance to allow more completely using a low molecular mass soluble fraction of lignin lost in the course of isolation, as well as reducing the consumption of reagents.

In our work we used black liquor taken from the Baikal pulp and paper mill with the following characteristics: pH 11.45, the mass fraction of dry solid residue 31.7 %, alkalinity (calculated for $Na_2O$) 20.3 %. The elemental composition of dry solid residue, %: C 37.3, H 2.9, Cl 0.5, S 3.2; ash 31.7. The mass fraction of lignin in the dry solid matter was equal to 22.9 %. For the synthesis of aminomethylated lignin,

TABLE 2

Characteristics of the synthesized aminomethylated lignins

| Samples | $R^1$ | $R^2$ | Elemental composition, % | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | | C | H | Cl | N | S | Ash |
| **L-1** hydrochloride | Me | Me | 57.27 | 6.05 | 6.20 | 3.05 | 3.83 | 1.84 |
| **L-2** | Me | Me | 63.76 | 6.46 | 1.68 | 1.68 | 1.98 | 0.67 |
| **L-3** | $(CH_2)_2OH$ | $(CH_2)_2OH$ | 59.97 | 6.36 | 0.12 | 1.14 | 2.01 | Отс. |
| **L-4** | Me | $(CH_2)_2OH$ | 62.60 | 6.91 | 0.42 | 3.16 | 1.68 | 0.52 |

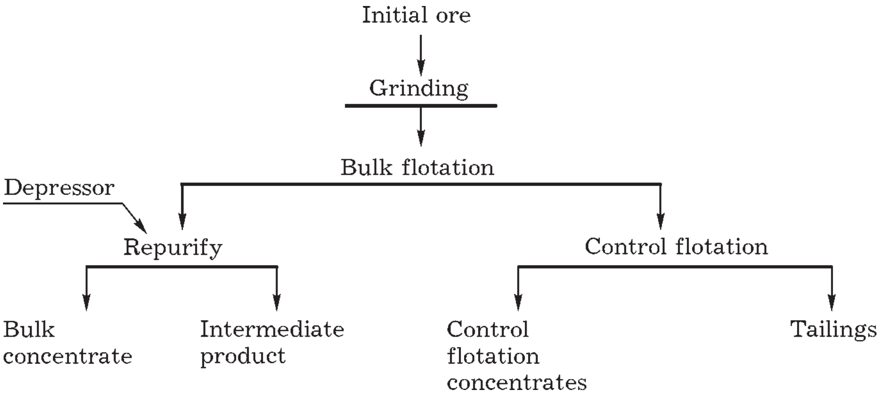


Fig. 1. Schematic diagram for the flotation of disseminated copper-nickel ore from the Norilsk-1 deposit.

the black liquor was mixed with an aqueous solution of formaldehyde and the appropriate amine and heated (80–85 °C, 4–5 h). The product was isolated *via* acidification of the reaction mixture up to pH 3–4. The features aminomethylated lignins are presented in Table 2.

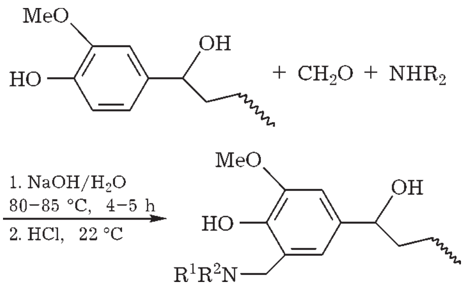
The laboratory scale investigations of using the reagents obtained as depressors performed according to the scheme demonstrated in Fig. 1.

The initial copper-nickel impregnation ore containing 0.52 % of nickel and 0.60 % of copper was grinded to obtain 55 % of −0.074 mm class. Further the ore was floated in an open cycle according to the collective scheme with the use potassium butyl xanthate (BKh) as a collector (150 g/t), and T-80 as a foam maker (100 g/t). The acid-base status of the medium (pH 9.3) was formed by means of soda (200 g/t). The concentrate obtained after the flotation was supplied to the purification operation where aminolignins **L-1**–**L-4** were tested as the depressors of non-metallic minerals.

The aminolignins tested were supplied for purification at a rate of 50 g/t (in the form of 0.5 % alkaline aqueous solution of the initial compound). For comparison, we involved CMC as a depressor in the operation of purification.

## RESULTS AND DISCUSSION

Lignins dissolved in the liquor (from softwood) predominantly have a guayacyl or 3,4-dihydro-substituted type of the ring where the potential reaction centre in the interaction with the formaldehyde–secondary amine system is located in the position 5 of the aromatic ring [6]:



In the molecule of sulphate lignin, approximately 33–40 % of phenolic units have free 5-position [7]. Under the experimental conditions (80–85 °C, 4–5 h), only a part of these centres is exposed to aminomethylation. The parameters of aminomethylated lignins used as depressor reagents are demonstrated in Table 2.

The IR spectra of the resulting products exhibit strong absorption bands at 3390–3435 $cm^{-1}$ corresponding to the stretching vibrations of OH and NH groups those are bound through intra- and intermolecular hydrogen bonds. Comparing with the original kraft lignin (sulphate lignin) a significant increasing the absorption band of methyl and methylene groups is observed within the range of valence (2923–2960, 2850–2877 $cm^{-1}$) and deformation (1350–1460 $cm^{-1}$) vibrations, whereas the intensity of the absorption band inherent in the carbonyl groups (1700 $cm^{-1}$) demonstrates a significant decrease or shifting towards lower frequency values. The group of weak absorption bands at 2700–2800 $cm^{-1}$ is caused by the vibrations of the free electron pair of the nitrogen atom.

In the course of the potentiometric titration of the modified lignin the differential curves demonstrate, as a rule, several maxima in the neutral zone, which indicates the presence of nitrogen-containing groups in the macromolecules as well as their interaction with the phenolic hydroxyl and carboxyl groups.

The aminolignin average molecular mass determined using gel filtration technique on Sephadex in dimethyl sulphoxide (DMSO) is equal to $16 \cdot 10^3$, which is slightly higher than that for the initial sulphate lignin. The molecular mass distribution of aminolignin is characterized by prevailing higher molecular mass fractions, the polydispersity level being equal to 1.8.

The ESR spectral signals for the modified lignin **L-1**–**L-4** represent singlets with the asymmetry parameter less than 1 and the width between the maximum slope points amounting to 0.60–0.64 mT, whereas the $g$-factor value is close to $g$-factor of free electron (2.0039–2.0050). The concentration of paramagnetic centres ranges within $(2.4–3.2) \cdot 10^{17}$ spin/g.

The results of disseminated ore flotation with the use of aminomethylated lignin as gangue depressor reagents are demonstrated in Table 3.

As far as the efficiency is concerned, the aminomethylated lignins are better as depressor reagents than the traditionally used depressor CMC in the flotation of disseminated ore of the Norilsk-1 deposit. Using the **L-2**–**L-4** samples in the purification operation of disseminated ore bulk flotation could improve the extraction efficiency to the bulk concentrate by

TABLE 3

Results of the flotation of disseminated copper-nickel ore (depressor consumption 50 g/t)

| Depressors | Flotation products | Yield, % | Content, % | | Extraction level, % | |
|---|---|---|---|---|---|---|
| | | | Ni | Cu | Ni | Cu |
| **L-1** | Bulk concentrate | 3.23 | 4.67 | 9.70 | 29.53 | 52.50 |
| | Middlings purifier | 4.36 | 2.71 | 2.47 | 23.15 | 18.06 |
| | Control flotation concentrate | 1.87 | 2.26 | 2.12 | 8.29 | 6.66 |
| | Tailings | 90.54 | 0.22 | 0.15 | 39.03 | 22.78 |
| | Initial ore | 100.00 | 0.51 | 0.59 | 100.00 | 100.00 |
| **L-2** | Bulk concentrate | 2.93 | 5.09 | 11.38 | 27.79 | 53.36 |
| | Middlings purifier | 4.33 | 2.95 | 2.62 | 23.80 | 18.15 |
| | Control flotation concentrate | 2.01 | 2.55 | 2.54 | 9.54 | 8.16 |
| | Tailings | 90.73 | 0.23 | 0.14 | 38.87 | 20.33 |
| | Initial ore | 100 | 0.54 | 0.62 | 100.00 | 100.00 |
| **L-3** | Bulk concentrate | 3.51 | 4.97 | 10.52 | 33.04 | 58.05 |
| | Middlings purifier | 4.14 | 2.61 | 2.39 | 20.47 | 15.56 |
| | Control flotation concentrate | 1.97 | 2.37 | 2.10 | 8.84 | 6.50 |
| | Tailings | 90.38 | 0.22 | 0.14 | 37.65 | 19.89 |
| | Initial ore | 100.00 | 0.53 | 0.63 | 100.00 | 100.00 |
| **L-4** | Bulk concentrate | 3.24 | 4.82 | 10.47 | 31.81 | 57.99 |
| | Middlings purifier | 4.17 | 2.78 | 2.51 | 23.63 | 17.90 |
| | Control flotation concentrate | 1.92 | 2.42 | 2.15 | 9.47 | 7.06 |
| | Tailings | 90.67 | 0.19 | 0.11 | 35.09 | 17.05 |
| | Initial ore | 100.00 | 0.50 | 0.58 | 100.00 | 100.00 |
| CMC | Bulk concentrate | 3.15 | 5.19 | 9.98 | 31.13 | 53.10 |
| | Middlings purifier | 3.34 | 2.92 | 2.15 | 18.54 | 12.11 |
| | Control flotation concentrate | 2.55 | 2.54 | 2.03 | 12.29 | 8.72 |
| | Tailings | 90.96 | 0.22 | 0.17 | 38.04 | 26.07 |
| | Initial ore | 100.00 | 0.53 | 0.59 | 100.00 | 100.00 |

0.68–1.91 % for nickel, as well as by 0.26–4.95 % for copper a compared with CMC. At the same time, a decrease is observed in the loss with the flotation tails: by 0.39–2.95 % for nickel, and by 3.29–9.02 % for copper. According to the analysis of the process parameters, the most efficient depressor is presented by sample **L-4** which is characterized by the highest content of active amino groups (3.16 %). Sample **L-1**, wherein the amino groups are protonated, exhibits the lowest activity and being less efficient than CMC.

## CONCLUSION

A convenient and technologically feasible method was developed for the rational utilization of lignin, a large-tonnage waste of pulp and paper industry based on the modification of lignin by *via* aminomethylation (Mannich reaction).

Using the aminomethylated lignin as a gangue depressor in purification operation of the bulk flotation of the disseminated ore from the Norilsk-1 deposit allows increasing the extraction level of nickel into bulk concentrate (by 0.68–1.91 %) and that of copper (by 0.26–4.95 %) as compared with the CMC.

The efficiency of novel depressor reagents is determined by the number of amino groups introduced into the lignin macromolecule.

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