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From amine molecules adsorption to amine precipitate transport by bubbles: A potash ore flotation mechanism ☆

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The paper is dedicated to the late Professor Jan Leja

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ABSTRACT

Recent investigations summarized in this review have been conveniently grouped into (i) those dealing with the mechanism of action of the reagents applied in the flotation of potash ores, and (ii) those focused on the flotation properties of salt-type minerals and explanation of the remarkable selectivity between floatable sylvite, and non-floatable halite. This paper is confined to the first group. It is argued that in discussing the mode of action of long-chain primary amines in the flotation of potash ores account must be taken of the way in which these amines are applied by industry. Because they are water insoluble they are melted by heating up to 70–90 °C and then they are dispersed in acidified aqueous solution. Once added to the flotation pulp, the hot amine dispersion rapidly cools down to a temperature far below the Krafft point. The rapid conversion from a hot emulsion to a cold precipitate is a very severe transformation. Since nothing is known about the kinetics of these changes and phase instability only the lab tests in which the adopted reagent preparation procedures closely follow the industrial practice have been considered in this review.

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1. Introduction

Applying flotation to treat ores containing water-soluble salts – as pointed out by Gaudin in his monograph (Gaudin, 1957) – was not considered until after Jeanprost (1928) showed that the flotation must be conducted in a saturated solution of such minerals. The minerals sylvite (KCl) and halite (NaCl), two major components of the most important potash ore – the sylvinite ore – can be separated by flotation that is carried out in a NaCl–KCl saturated brine. At 20 °C, 1.450 kg of the KCl–NaCl saturated solution contains about 0.300 kg of NaCl, 0.150 kg of KCl and 1 kg of water (Gaska et al., 1965). Thus the NaCl–KCl saturated brine is approximately 6 mol/L solution of these two salts. The NaCl concentration

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☆ Based on 2010 Gaudin lecture which was presented at the SME Annual Meeting, Denver, February 28, 2011.

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in seawater is about 0.6 M, there is thus a huge difference in the electrolyte concentrations between potash ore flotation pulps and pulps in other flotation operations. Only now is it becoming apparent that dissimilarity between the potash ore flotation and other flotation systems results mostly from differences in the ionic strength.

This paper reviews recent advances made in understanding the nature of phenomena taking place in the flotation carried out in NaCl + KCl saturated brine, that is in the potash ore flotation process. The purpose of this paper is to draw a common thread through seemingly disparate pieces of evidence, and to reconcile various experimental results and various theories put forward in the area of potash ore flotation.

For the sake of discussion, the papers dealing with various aspects of potash ore flotation have been grouped into:

(i) Those which discuss the mechanism of action of long-chain flotation collectors in saturated brine that leads to a good flotation of KCl in such an environment.
(ii) Those studying the differences between flotation properties of various water soluble salts which make some of them floatable while the others are not.

The latter group will not be considered in this review, the reader is referred to several excellent publications on this topic. Rogers and Schulman (1957) and Rogers (1957) were the first to consider hydration as the phenomenon responsible for the surface properties of alkali halides. They pointed out that ions like Na^+, K^+, and Cl^-, etc., are strongly hydrated and that the properties of the surfaces of the minerals containing such ions in water are to a large extent determined by these ions' hydration. This model was further developed by Miller et al. (Hancer et al., 2001; Cao et al., 2010; Cao et al., 2011; Ozdemir et al., 2011), who were able to show that hydration phenomena at salt crystal surfaces provide a good explanation for the flotation properties of floatable sylvite and non-floatable halite (advancing contact angle on KCl was measured to be 7.9 ± 0.5° while such an angle measured on NaCl was 0°). The differences in the hydration between KCl and NaCl surfaces is believed to affect the adsorption of flotation collectors on these salts.

2. Early research

It was not until the 1950s that the first detailed papers on the adsorption of aliphatic amines on halides were published by Fuerstenau and Fuerstenau (1956) – papers that represent the beginning of scientific research on the flotation fundamentals of potash ores. In this flotation process, two isomorphous minerals – sylvite and halite – are separated by flotation. The best separation between these minerals, which differ only in the cation, are obtained with cationic collectors.

The only interpretation that makes sense (Gaudin, 1957) is that the ammonium ion fits in the place of potassium at the sylvite surface but does not fit in the place of sodium at the halite surface. Fig. 1 shows schematically the mechanism proposed by Fuerstenau and Fuerstenau (1956).

Some of the benchmarks in the development of the potash ore flotation process are listed in Table 1. While the author has tried to tabulate all important developments in this area, only those that are consistent with the view presented in this paper will be discussed further. The list begins with Kirby's patent (US Patent 2,088,325), which introduced straight-chain primary amines into the technology of potash ore flotation as a universal collector.

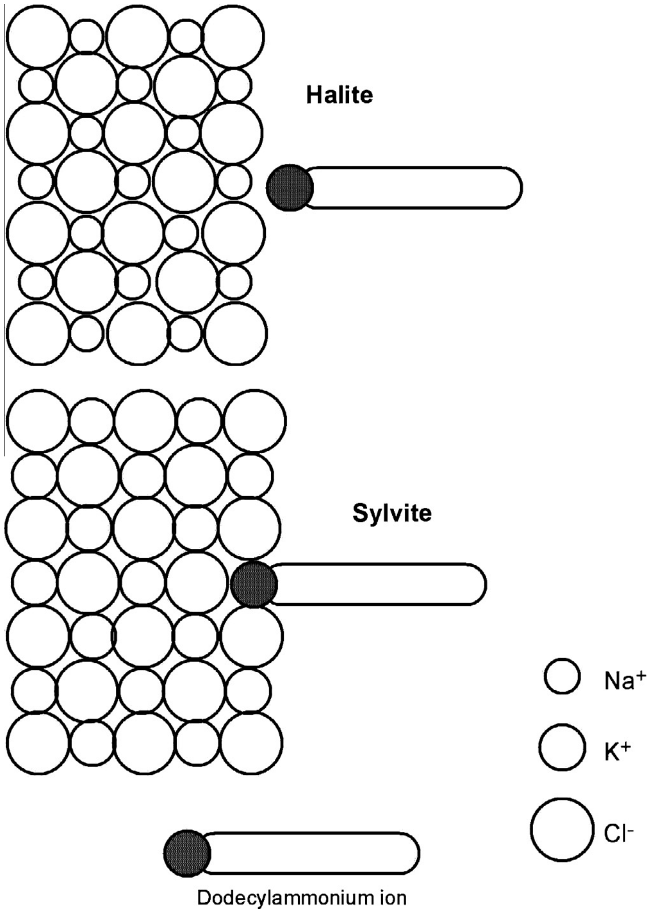

Fig. 1. Schematic representation of the mechanism of collection of sylvite and lack of collection of halite by dodecylammonium ions (D.W. Fuerstenau and M.C. Fuerstenau, 1956).

Table 1
Some important contributions in the area of potash ore flotation.

Year	Contributors
1937	J.E. Kirby
1956	D.W. Fuerstenau, M.C. Fuerstenau
1957	J. Rogers, J.H. Schulman
1951–1988	R. Bachman, A. Singewald, H. Schubert
1968	R.J. Roman, M.C. Fuerstenau, D.C. Seidel
1977–1982	J. Leja, V.A. Arsentiev
1985	D.A. Cormode
1988	V.A. Arsentiev, T.V. Dendyuk, S.I. Gorlovski
1982 – present	S.N. Titkov
1990 – present	J.D. Miller and co-workers
1986 – present	J.S. Laskowski and co-workers

Many ideas – especially in the early period of the process' development were more or less directly transplanted from other flotation processes. However, a comparison of some fundamental correlations found in froth flotation, for example the relationship between collector concentration and recovery, for the common flotation systems and the potash ore flotation system is stunning. It is known that the recovery curve, plotted versus collector concentration, drops to zero when collector concentration approaches the critical micelle concentration. This is shown in Fig. 2.

As Fig. 2 demonstrates, whenever the collector concentration approaches the critical micelle concentration, micelles appear in the solution and flotation drops to zero. This is not surprising since micelles are colloidal hydrophilic entities and their accumulation on the mineral surface must render such a surface hydrophilic.