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Flotation Reagents: Applied Surface Chemistry on Minerals Flotation and Energy Resources Beneficiation

Volume 1: Functional Principle

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Preface

The development of minerals processing over one hundred years has shown flotation a predominant process of materials separation. Nowadays, flotation is widely used in minerals separation, treatments of slag and wastes, materials separation, and valuables recovery in metallurgical, coal, and chemical engineering. Flotation reagents have played vital roles in the progress of flotation process. The development and application of the reagents have made it possible for more and more traditional refractory ores and materials to be treated by flotation process with high efficiency.

Several books on flotation principles and reagents have been published, however, for further improvement of current minerals processing performance and for the treatment and recovery of refractory and nontraditional mineral and energy resources, scientists need to develop new reagents and innovative processes.

The author of this book took up investigation of flotation reagents in the 1960s. The fundamentals and approaches of surface chemistry have been applied in the round to discuss the structure, performance of the reagents, and the interaction between the reagents and minerals, as well as to set up theoretical criteria for collector performance. Molecular orbit method incorporating with molecular design was used to have obtained quantum chemistry parameters, steric configuration, HOMO, and LUMO surface of various reagents. This book has summarized the results that the author has achieved on functional principle of flotation reagents in the last 50 years.

The Chinese edition of this book was published in 1982 and reprinted in 1994 by Metallurgical Industry Press. This English edition, on the basis of Chinese edition, has incorporated the new findings on the topic in particular the molecular design of reagents achieved by the author and his research group. This book is intended for worldwide university teachers, researchers, R&D engineers, and graduate students in minerals processing, extractive metallurgy, and resources utilization who wish to explore innovative reagents and technologies that lead to more energy efficient and environmentally sustainable solutions.

In time of publication of the English edition, I would like to acknowledge cooperation and contributions to the contents of this book from my colleagues and graduate students. A special acknowledgment is warranted to Dr. Guihong Han, who completed the onerous translation of this book with his dedication and persistence. I give my sincere thanks to Prof. Tao Jiang, who undertook the proposal for the publication and helped to review the first draft. Thanks also to Mr. Xiaofeng Liu (editor of Metallurgical Industry Press), who encouraged and helped to complete this project.

Beijing, China Dianzuo Wang
December 2015

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Chapter 1
Introduction

1.1 Brief History of Research and Application of Flotation and Reagents

Flotation is one of the mineral processing methods according to the difference of surface hydrophobicity and hydrophilicity of minerals. Although part of ores can be beneficiated based on their natural hydrophobicity, most of them need the addition of various reagents into the ore pulp for selectively controlling the hydrophobicity and flotation behaviors of minerals and for achieving satisfactory separation results. Therefore, flotation reagents are important for the application and the development of flotation technology.

The application of flotation technique and reagents in the mineral processing can date back to ancient times. The early flotation process was quite simple and was mainly film flotation based on natural hydrophilicity or flotability of minerals. Taking the beneficiation of talc and kaolin for example, there were four major steps such as washing, sinking, floating, and pouring. Those steps include not only gravity separation but film flotation. The record on this kind of processes can be found from the book "Heavenly Creations," written by Ying-Hsing Sung, a famous scholar of Ming dynasty of China in sixteenth century. The book described the flotation process of cinnabar as follows: (1) Firstly, grinding the ore into fine powders in a large metal trough; (2) Secondly, soaking fine powders with clear water in a water tank; (3) Then for three days, the suspension called second-class cinnabar were poured from water tank to another one; (4) Finally, sedimented particles called top-class cinnabar were dried.

Later on, people utilized flotation reagents alike with these used today, which may be unconscious in the beginning. There were numerous examples for the application of various reagents to mineral flotation. In the processing and purifying of painting pigments (covellite, cinnabar, and so on), for instance, animal glue was added to the ore suspension to improve the adhesivity. The protein, amino acid, and their polymers in animal glue can act as collector, depressant, and flocculant, and

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therefore affect the process of "grinding, soaking, floating, and sinking." For another instance, medicinal plants were often added into the minerals pulp and cooked together before elutriation in the processing and purifying of mineral medicinal substances (realgar, orpiment, talc, cinnabar, etc.). In the process, organic acids, organic bases, alcohols, and various oils coming from those plants could perform as flotation reagents. These examples were common occurrences in the "Compendium of Medica," which was written by Shizhen Li in Ming Dynasty. The book recorded the flotation processing of ruddle and realgaras in detail.

Since ancient times, a process called "scratching gold by goose feather" was used in the beneficiation of gold from placer gold. In the course of panning placer gold, the goose feather was dipped with plant oil for bonding fine gold particles. In fact, this was the special flotation with oils and fats as collectors. There was also description about the so-called oil agglomeration of fine particles in the book of "Heavenly Creations." When golden foil ornaments were worn out and broken, they were scraped off and burned in the fire and the gold particles would be in ashes. Adding water and some drops of oil, the oil agglomerates with gold formed and fell in the bottom and were put to the metallurgical furnaces. This is probably the earliest description about selective agglomeration for fine gold particles.

According to records, William Haynes in 1860s patented a process for separating sulfide and gangue minerals using oil and it was called bulk oil flotation. The modern froth flotation process was invented in the late 1900s [1, 2]. Froth flotation technology was used initially for treating lead–zinc ore and then expanded into the treatment of other nonferrous metal, rare metals, iron ore, and nonmetallic minerals. Statistics show that flotation accounts for the greatest share among currently used methods in mineral processing. And the share will increase in the future. In addition to the beneficiation of ores, flotation technology has been gradually adopted for treating various industrial wastes and applied in the areas of agriculture and light industry.

The research and the application of flotation reagents continue to advance with the development of flotation technology. In briefly, the development of flotation reagents mainly includes three stages.

The first stage is the period of oil reagents. In the beginning of flotation industrialization, various mineral oils and plant oils, such as coal tar and paper tar, were used as flotation reagents. These flotation reagents consist of hydrocarbon oils, fatty oils, and some organic matters. Because of being water-insoluble and weak interaction with minerals, those reagents were used in high dosage. Subsequently, people began to process oils to improve the properties of oil reagents. The early so-called processing oil means that coal tar oil is thermally treated with sulfur, acids, or alkali, or treated with carbon disulfide, or sulfur monochloride. Because of containing a given mass of water-soluble organic sulfides, phenolates, and pyridinium salts, the processed oil owns better flotation performance than the crude oil. For example, the sulfurated anthracene oil once used as the substitute for xanthate in China is a typical representative of processed oils. Then flotation scientists began to realize that the crude oil is not the excellent reagents. But the water-soluble "impurity" (organic compounds containing nitrogen or sulfur) usually performs excellent collecting property. That may be the earliest knowledge about the structure and performance of flotation reagents.

The second stage is the period of artificial synthesis of water-soluble flotation reagents. The water-soluble frothers were firstly applied in 1909. Fatty acid soaps were used in the flotation of nonsulfide minerals in 1924. Xanthates were used as collector in 1925. Cyanide, acids, and alkali were utilized as regulators in succession from 1922 to 1929. These reagents are all artificial synthesis or modified products of natural products. Because of a higher proportion of water-soluble active ingredients, the utilization of these reagents has turned flotation into a process of low consumption, low cost, high efficiency, and wide application.

Meantime, the theory of flotation reagents was much improved. The flotation reagents had been classified in accordance with their different roles. Various theories, hypotheses about flotation reagents were proposed to guide or improve flotation processes and search for new reagents. Among these theories and hypothesis, the solubility product hypothesis proposed by Taggart produced a great impact. As for searching for reagents, the hypothesis can be briefly described as follows: Reagents which can form low solubility product compound with mineral component, and at the same time possesses the structure characteristic of flotation reagent, may act as collectors and depressants. Although this hypothesis is imperfect, it is still used not only for the analysis of flotation phenomenon but also as one of criteria searching for new reagents.

The third stage is characterized by further expansion of reagent variety and raw material source for production of new reagents. The development of mining industry and the requirement of science and technology for mineral raw materials make new demands on types and quantity of flotation reagents. Meantime, the development of petroleum industry provided various structural and cheap, wide raw materials for reagent development, resulting in diversification of flotation reagents. For example, xanthate, including *n*-alkanol ethyl xanthate, *n*-alkanol butyl xanthate, was extended to isopropyl xanthate, isobutyl xanthate, isoamyl xanthate, and so on. Lots of special-purpose and high efficiency reagents were developed and used in order to treat various rare metal ores, polymetallic ores, low grade and fine ores, and oxidized ores, which include all kinds of collectors, depressants, and high selectivity flocculants. Frothers are also gradually used from petroleum products, which in past were main terpene alcohols made from natural plants.

It is worth mentioning that water-insoluble and high effective oily collectors were also developed in recent years. For example, these collectors involve thionocarbamates, xanthate esters, and dithiophosphates. And these reagents possess the characteristic of low dosage (1/5–1/10 dosage of xanthate) and high efficiency. The theory of flotation and reagent was improved much more in this period. Because of the application of various testing techniques and advancement of modern physical chemistry, surface chemistry, electrical chemistry, structural chemistry, and quantum chemistry, many flotation fundamentals associated with reagents were well elucidated.

Recent years, the advances in the areas of material molecular design pave a way for development of new flotation reagents. The theory of molecular design may