SAMPLING AND ANALYSIS OF COPPER CATHODES

A symposium
sponsored by ASTM
Committee B-2 on
Nonferrous Metals and Alloys
Dallas/Fort Worth, Tex., 16–17 Nov. 1982

ASTM SPECIAL TECHNICAL PUBLICATION 831
W. M. Tuddenham, Kennecott Minerals Company,
and R. J. Hibbeln, Western Electric Company,
editors

ASTM Publication Code Number (PCN)
04-831000-03

1916 Race Street, Philadelphia, Pa. 19106

Library of Congress Catalog Card Number: 83-72433

NOTE

The Society is not responsible, as a body,
for the statements and opinions
advanced in this publication.

Printed in Baltimore (b)
March 1984

Foreword

ASTM Symposium on Sampling and Analysis of Copper Cathodes was held 16–17 November 1982 in Dallas/Fort Worth, Texas. The event was sponsored by ASTM Committee B-2 on Nonferrous Metals and Alloys. W. M. Tuddenham, Kennecott Minerals Company, and R. J. Hibbeln, Western Electric Company, served as symposium chairmen and have edited this publication.

Related ASTM Publications

Sampling, Standards, and Homogeneity, STP 540 (1973), 04-540000-34

A Manual on Methods for Retrieving and Correlating Technical Data, STP 468 (1969), 04-468000-41

Formability of Metallic Materials—2,000 A.D., STP 753 (1981), 04-753000-23

United Numbering System for Metals and Alloys and Cross Index of Chemically Similar Specifications, DS 56B (1983), 05-056002-01

A Note of Appreciation to Reviewers

The quality of the papers that appear in this publication reflects not only the obvious efforts of the authors but also the unheralded, though essential, work of the reviewers. On behalf of ASTM we acknowledge with appreciation their dedication to high professional standards and their sacrifice of time and effort.

ASTM Committee on Publications

ASTM Editorial Staff

Contents

Analysis

Summary

Introduction

The papers included in this publication were prepared for the Symposium on Sampling and Analysis of Copper Cathodes held on 16–17 November 1982 in Dallas/Fort Worth, Texas. Sponsored by ASTM Committee B-2 on Nonferrous Metals and Alloys, this symposium was the first public international forum addressing the subject of analytical problems relating to high-purity copper cathodes. The new high-purity cathodes are required by producers of continuous cast copper rod. Representatives of seven countries attended. Papers were presented which reported the findings of individuals who have been studying these problems in sampling and analysis.

In creating the symposium, the sponsoring committee recognized that international attention was being directed toward selecting the best methods of sampling and analyzing electrolytic copper cathode. As R. L. Dana, the author of "Sampling and Analysis in the Production and Consumption of Copper Cathodes," so ably writes, "The major problem that currently faces both the cathode producer and the consumer is the necessity to confirm specification compliance before universally accepted cathode sampling and analytical methods have been adopted. This dilemma will undoubtedly make the disputes over cathode quality more difficult to resolve." Hoping to contribute to a resolution of these problems, the symposium sponsors encouraged the efforts of individual investigators, invited them to present their findings, and published their papers, thereby making an exchange of information possible.

The papers are arranged in three groups: overview, sampling, and analysis. Taken together these papers constitute a fairly comprehensive review of current investigations by those in the field.

A general overview of current practices is provided by the first group, which helps define the problem and presents various viewpoints on sampling and analytical methods. These papers include a review of the current scene by a major U.S. producer, the practices of a large U.S. consumer in operating their continuous cast copper rod mill, and a progress report by the British Non-Ferrous Metals Federation on their work with others in Europe toward the development of methods for sampling and analysis.

The second and largest group of papers, on cathode sampling, yields abundant information. The authors report on investigations into drilling, punching, strip sectioning, milling, and saw cut procedures for obtaining samples. Data on the distribution of impurities within a cathode and variations from cathode to cathode and from lot to lot are reported and interpreted. Studies on lot and sample sizes are also treated.

The papers in the analysis group provide information on methods of determining impurity levels and the accuracy of those methods. A paper from the National Bureau of Standards outlines the development of Benchmark Standards and Standard Reference Materials of copper with trace impurities for use as standards by chemical laboratories. Also included are papers reviewing the precision of current analytical practices in relation to the new high-purity requirements and reporting studies with a newer technique, argon direct-current plasma atomic emission, which has potential for future applications.

The publication of these papers should prove useful as the copper industry strives to meet the challenge of adjusting analytical methods for confirming compliance to new specifications. It is important also to reflect here on the changes which prompted the sponsoring committee to address this problem.

Specifications were recently issued to include new requirements for high-purity grades of copper cathodes and to specify maximum composition limits for impurities. These new specifications resulted from demands for higher purity by cathode consumers producing continuous cast copper rod.

Several changes regarding specifications have been made. One was a revision of ASTM Specification for Electrolytic Cathode Copper (B 115) that was approved by ASTM membership in 1982. The revision established a new Grade 1 cathode. In Europe, the International Wrought Copper Council (IWCC) working with the British Non-Ferrous Metals Federation and through several international meetings of producers and consumers developed specification requirements for a high-purity copper cathode on which London Metal Exchange (LME) contracts are based. These two major specifications differ in chemical composition requirements.

A major recognized obstacle in each of the foregoing specifications is the difficulty of establishing an agreed referee method for sampling and analysis. For instance, ASTM B 115 contains this statement, "8.2.1 Until ASTM methods of analysis have been established, the analytical, sampling, and sample preparation methods for determining the composition of Grade 1 shall, in case of disagreement, be as agreed upon between the manufacturer and the purchaser." Also, the specification used in the LME contract was issued as a tentative British standard (Draft for Development DD 78) which can be converted to a full British standard when methods for sampling are agreed upon.

The International Standards Organization, Technical Committee 26 (ISO/TC 26), at its October 1980 meeting in Orlando, Florida, passed resolutions to create two working groups to study sampling and analysis of copper cathodes. When the working groups complete the assignment, ISO/TC 26 plans to proceed with the development of chemical composition requirements in a specification for high-purity copper cathodes.

Obviously the road to consensus agreements is not clearly mapped nor can the time to travel its distance be predicted. The work reported here, however, will provide the copper cathode industry with guideposts for future work toward the development of agreed methods to serve producers and consumers of copper cathode using ASTM and other standards. Further, this publication is a valuable source of reference and information for all who are working on cathode sampling and analysis problems.

The editors wish to acknowledge the many individuals who have contributed in several ways to create the outstanding symposium and to make this publication a reality. These supporters have found time in their busy work schedules to volunteer generously and enthusiastically in providing cooperation and assistance in this endeavor.

A vital part of the project was having the authors and presenters share with us their investigations, data, information, and interpretations. Many qualified individuals also gave support by reviewing the papers before publication. We are most grateful for the support and efforts of the authors, presenters, and reviewers.

The guiding hand of the moderators at the symposium was responsible for the program progressing smoothly and on schedule. For this effort and other support a special thanks is given to Arthur Cohen, Copper Development Association, and Martha Mathews, Cyprus Bagdad Copper Company. The panel members at the symposium—P. R. Soriano, AMAX; M. V. Yokelson, General Cable Company; C. J. Roesch, Western Electric Company; C. M. Wolpert, ASARCO; and D. H. Butler, British Non-Ferrous Metals Federation—are given praise and thanks for presenting their views reflecting the years of experience and commitment to their special areas.

We are also very grateful for the support of the publication staff at ASTM. Finally, without ASTM Subcommittee B02.01 on Refined Copper initiating the idea and without the sponsorship by ASTM Committee B-2, this event would never have happened.

W. M. Tuddenham
Kennecott Minerals Company, Salt Lake City, Utah; symposium chairman and editor.

R. J. Hibbeln
Western Electric Company, Chicago, Illinois; symposium chairman and editor.

Overview

Richard L. Dana[1]

Sampling and Analysis in the Production and Consumption of Copper Cathodes

REFERENCE: Dana, R. L., "**Sampling and Analysis in the Production and Consumption of Copper Cathodes,**" *Sampling and Analysis of Copper Cathodes, ASTM STP 831,* W. M. Tuddenham and R. J. Hibbeln, Eds., American Society for Testing and Materials, 1984, pp. 7–15.

ABSTRACT: New high-grade cathode specifications are including specific impurity limits to meet the more stringent requirements of the continuous cast rod market. Improved cathode sampling and analytical methods are necessary to confirm specification compliance. A better sampling plan is to collect either saw cuttings or cut sections from the cathodes which would then be melted and cast to obtain adequate impurity representation. Interest in obtaining lower impurity detection limits is leading to more support for the electrothermal and vapor generation methods of atomic absorption spectrometry. Even after the improved methods of sampling and analyzing copper cathodes have been tested and adopted, frequent interaction between the cathode producer and consumer will be important to monitor product quality compliance.

KEY WORDS: product specifications, continuous cast rod, cathodes, impurity behavior, electrolytic refined copper, sampling, analysis, cathode marketing

International attention is being directed toward selecting the best methods of sampling and analyzing electrolytic-refined copper cathodes. An accurate assessment of cathode quality has become extremely important, since consumers are requiring a higher grade product for their continuous cast rod applications. The recently introduced cathode specifications now place specific concentration limits on those impurities that primarily affect either the annealing or electrical conducting properties of the fabricated copper products.

The major problem that currently faces both the cathode producer and the consumer is the necessity to confirm specification compliance before universally accepted cathode sampling and analytical methods have been adopted. This dilemma will undoubtedly make disputes over cathode quality more difficult to resolve.

[1] Supervisor, Analytical Research Laboratories, Anaconda Minerals Company, Tucson, Ariz. 85726.

Impurities in the cathodes have the tendency to be significantly heterogeneous. This paper will discuss the reasons for this impurity nonuniformity in order to emphasize the complexities of obtaining a representative sample. Once the cathode samples have been taken and prepared, selecting universally accepted analytical methods becomes the next important step. The advantages and disadvantages of commonly used instrumentation techniques will be presented.

Electrolytic-Refined Copper Cathode Production

The production of copper cathodes in a tankhouse represents the last step in a series of processes that lead to a marketable product for the consumers. Each of the major processes (Fig. 1) can influence the quality of the cathode. Depending upon the type and amount of impurities present in the orebody, attention must be given to their necessary separation or control. Treatment

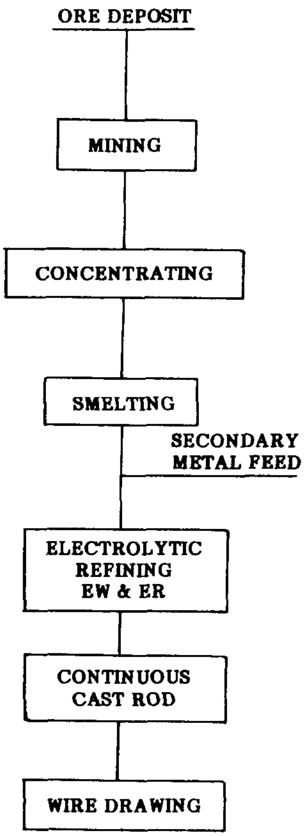

FIG. 1—*Operational processes in copper production.*

TABLE 1—*Cathode impurities characteristic of different tankhouse operations.*

Tankhouse Operation	Cathode Impurities
Electrowinning	S, Pb, Fe
Electrorefining	Ag, Se, Te, As, Sb, Bi, Pb, S

of the copper concentrate by either hydro- or pyrometallurgical methods has an influence upon which impurities commonly reach the tankhouse. Table 1 shows more detrimental cathode impurities that are specifically characteristic of electrowinning or electrorefining operations.

The anode composition and the behavior of the dissolved or precipitated impurities in the electrolyte influence cathode quality. Depending on their respective densities, the precipitated constituents tend to localize on the upper edge or at the bottom section of the cathode.

Nodular cathode surfaces can cause severe heterogeneous occlusions of the precipitated impurities. As shown in Figure 2, the extent of impurity occlusions is considerably less eminent in Cathode A than in Cathode B.

Cathode surfaces will have to be free of nodulation in order for the impurities to be below the new high-grade specifications shown in Table 2. The commonly obtained and preferred impurity ranges, which are also shown in Table 2, will undoubtedly lead to a more uniform distribution of impurities in the cathode; however, in all cases, obtaining a representative sample is essential to evaluating specification compliance.

Cathode Sampling Methods

Cathode sampling involves three basic steps:

1. Random selecting of an adequate number of cathodes that are representative of a lot.
2. Obtaining a sample from the random-selected cathodes through a mechanical process such as drilling or sawing on a prescribed pattern.
3. Preparing a homogeneous portion from the sampled cathodes that is of suitable size and quantity for chemical analysis.

The number of cathodes that must be sampled to represent a lot is dependent upon the size of the lot and upon the respective cathode quality. Many reports have addressed the subject of lot representation; however, the data must be reassessed in terms of the new high-grade specifications. Further statistical studies should be conducted when standardized cathode sampling and analytical methods have been developed. The importance of a widely accepted method of sampling cathodes cannot be overstated.

A comparison of the different approaches to cathode sampling is shown in Table 3.