Navin G. Ashar · Kiran R. Golwalkar

A Practical Guide to the Manufacture of Sulfuric Acid, Oleums, and Sulfonating Agents

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To the hundreds of scientists, engineers,
workers, and technocrats who have
contributed significantly towards
the development of knowledge and
technology for more efficient, safe,
and environment-friendly working
of these industries; and who will
continue to do so in future.

Preface

It gives us great pleasure to present this monograph for use and reference by design, development, production, and maintenance engineers, managements and all those associated with the industries manufacturing sulfuric acid and sulfonating agents.

This book attempts to update and compile the information and experience generated on the technology of manufacture of these chemicals over the last few decades, after earlier treatment of this subject by Andrew M. Fairlie in the 1940s and by Werner W. Duecker and James R. West in the 1960s.

These industries are vital for the technical and economic progress of any country—a fact which has been well acknowledged throughout the world. Even though the chemical reactions involved in production of these chemicals are well known and the technologies for their manufacture are well established, we have made an attempt to compile and *update* the information available.

This attempt is to compile the latest state-of-the-art on sulfuric acid and sulfonating agents based on our own experience for the design, erection, commissioning, operation, and maintenance of production plants as well as the experience of many well known industries and knowledgeable people in the field. In addition, we have attempted to highlight the important technical issues for future development, smooth and safe plant operation, and economic viability in view of the rising raw material and energy costs globally.

We have taken due note of standard works on the subject such as 'The Manufacture of Sulfuric Acid' by Werner W. Duecker and James R. West, 'Sulfuric Acid Manufacture' by Andrew M. Fairlie, 'Encyclopaedia of Chemical Technology' by Kirk and Othmer, 'Sulfuric Acid Manufacture' by King, Moats, and Davenport, 'Handbook of Sulfuric Acid Manufacture' by D.K. Louie as well as information available through websites of reputed manufacturers and technology suppliers for sulfuric acid plants and equipment required for the same.

It is hoped that the practising personnel and management will find the book useful for improving plant efficiency, safety, environment, diversification to value added products such as liquid SO_2 and SO_3, expansion of capacity, profitability, etc., and will be able to contribute significantly to the progress in the state-of-the-art in sulfuric acid industry.

We also hope that this monograph will stimulate creative thinking for further all-round development.

We welcome creative suggestions from knowledgeable experts for updating the improvements in this field and due acknowledgement of these will be incorporated in future editions.

The publication of this book has been made possible with very active and valuable help from the NEAT team.

Mumbai, India Navin G. Ashar
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Current Status of Manufacture of Sulfuric Acid

1

1.1 Introduction

1.1.1 History of Sulfuric Acid

Sulfuric acid was known to medieval alchemists under a variety of names including *oil of vitriol* and *spirit of vitriol*. These substances were produced by the dry distillation of minerals including iron (bivalent) sulfate heptahydrate, $FeSO_4•7H_2O$ known as green vitriol and copper (bivalent) sulfate pentahydrate, $CuSO_4•5H_2O$ known as blue vitriol. When heated, these compounds decompose into iron and copper oxides, respectively, giving off water and sulfur trioxide, the two of which combine to produce a dilute solution of sulfuric acid. Preparations like these have been ascribed to alchemists including the twelfth century Arab Abou Bekr al-Rhases and the thirteenth century German Albertus Magnus.

In the seventeenth century the German-Dutch chemist Johann Glauber prepared sulfuric acid by burning sulfur together with saltpeter (potassium nitrate, KNO_3) in the presence of steam. As the saltpeter decomposes, it oxidizes the sulfur to SO_3, which combines with water to produce sulfuric acid. In 1736, Joshua Ward, a London pharmacist, used this method to begin the first large-scale production of sulfuric acid.

In 1746 in Birmingham, John Roebuck began producing sulfuric acid this way in lead-lined chambers, which were stronger, less expensive, and could be made larger than the glass containers which had been used previously. This *lead chamber process* allowed the effective industrialization of sulfuric acid production, and with several refinements remained the standard method of production for almost 2 centuries.

John Roebuck's sulfuric acid was only about 35–40% sulfuric acid. Later refinements in the lead-chamber process by the French chemist Joseph-Louis Gay-Lussac and the British chemist John Glover improved this to 78%. However, the manufacture of some dyes and other chemical processes require a more concentrated

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product, and throughout the eighteenth century this could only be made by dry distilling minerals in a technique similar to the original alchemical processes. Pyrite (iron disulfide, FeS_2) was heated in air to yield iron (bivalent)sulfate, $FeSO_4$, which was oxidized by further heating in air to form iron (trivalent)sulfate, $Fe_2(SO_4)_3$, which when heated to 480 °C decomposed into iron (trivalent)oxide and sulfur trioxide, which could be passed through water to yield sulfuric acid in any concentration. The expense of this process prevented the large-scale use of concentrated sulfuric acid.

In 1831, the British vinegar merchant Peregrine Phillips patented a far more economical process for producing sulfur trioxide and concentrated sulfuric acid. In this process, sulfur dioxide, SO_2, produced by roasting either sulfur or pyrite in air, is combined with additional air and passed over a platinum catalyst at high temperatures, where it combines with oxygen from the air to produce nearly pure SO_3. Even so, there was little demand for highly concentrated sulfuric acid at the time, and the first sulfuric acid plant using this *Contact Process* was not built until 1875 in Freiburg, Germany.

The development of the less expensive and less easily contaminated vanadium pentoxide (V_2O_5) catalyst by BASF in Germany in 1915, combined with increasing demand for concentrated sulfuric acid by the chemical industry, has led to the gradual replacement of the lead-chamber process by the Contact Process. In 1930, sulfuric acid produced by the Contact Process accounted for only 25% of sulfuric acid production, while today nearly all sulfuric acid is manufactured in this way.

The conversion of SO_2 to SO_3 takes place by the reversible exothermic reaction

$$2\mathrm{SO}_2 + \mathrm{O}_2 \leftrightarrow 2\mathrm{SO}_3 \Delta\mathrm{H} = -22.93\,Kcal/\mathrm{gMole}$$

While the rate of the forward reaction increases with temperature, the equilibrium conversion decreases (thus reducing the yield of SO_3).

The Contact Process was further modified to the Double Contact Double Absorption process, which uses Le Chatelier's principle. According to this, when the SO_3 produced (as a result of conversion of SO_2 by the catalytic process) is absorbed by the intermediate absorption towers, the equilibrium conversion shifts to the right, i.e., more SO_2 is converted to SO_3. This is accomplished by reheating and then passing the reaction gases through an additional bed of catalyst. The SO_3 produced (additionally) is then absorbed in a second absorption tower.

[See Flow Diagram (3+2) DCDA process].