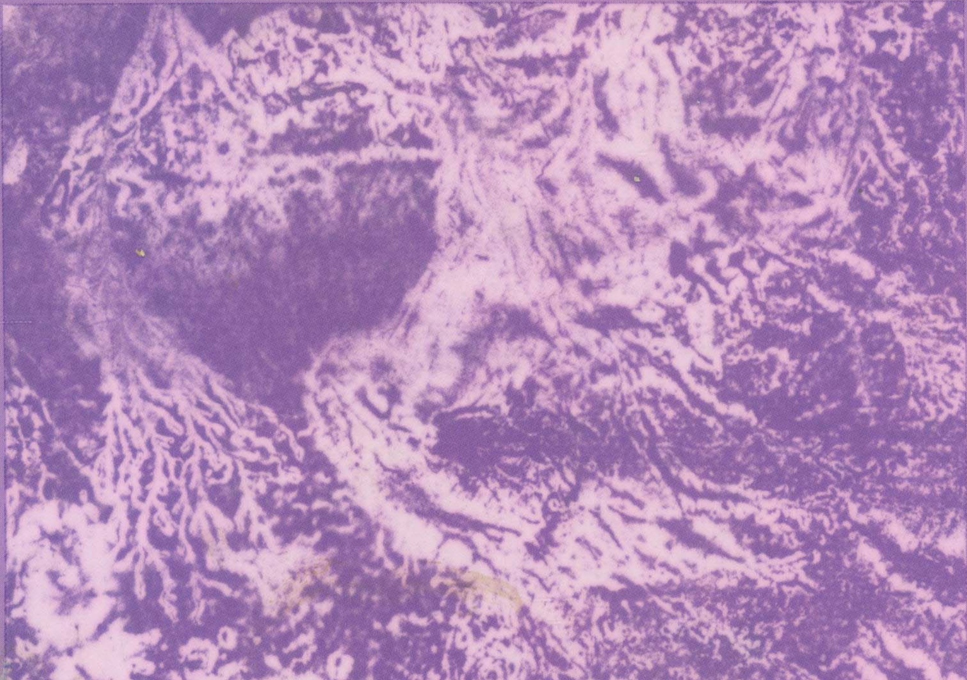
CAKE FORMATION IN PARTICULATE SYSTEMS

EDWARD J. GRIFFITH



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Library of Congress Cataloging-in-Publication Data

Griffith, Edward J.
Cake formation in particulate systems / by Edward J. Griffith.
p. .cm.
Includes bibliographical references and index.
ISBN 0-89573-748-5
1. Particles. 2. Agglomeration. I. Title.
TP156.P3G75 1991
660′.293—dc20 91-7709
CIP

British Library Cataloguing in Publication Data

Griffith, Edward J.
Cake formation : the applied chemistry of cake formation
in particulate systems.
1. Particulate solids
I. Title
660.2842

ISBN 3-527-27844-3

ISBN 0-89573-748-5

Printed in the United States of America.

ISBN 0-89573-748-5 VCH Publishers
ISBN 3-527-27844-3 VCH Verlagsgesellschaft

Printing History:
10 9 8 7 6 5 4 3 2 1

Published jointly by:

VCH Publishers, Inc.
220 East 23rd Street
Suite 909
New York, NY 10010

VCH Verlagsgesellschaft mbH
P.O. Box 10 11 61
D-6940 Weinheim
Federal Republic of Germany

VCH Publishers
(UK) Ltd.
8 Wellington Court
Cambridge CB1
1HW
United Kingdom

DEDICATED

TO

PROFESSOR HAROLD E. WILCOX

WHOSE TEACHINGS ARE FOUND THROUGHOUT THIS BOOK

PREFACE

THE APPLIED CHEMISTRY OF CAKE FORMATION IN PARTICULATE SYSTEMS

A Generalized Description

Cake formation in solid products is so common that hardly anyone is immune to the problems that cake formation can cause. It may be as simple as salt that will not flow from a salt shaker to the return of an entire warehouse of finished goods to the manufacturer because his product has become one gigantic lump.

Solids cake and form lumps for a wide variety of reasons, but most caking phenomena can be classified under one of four major types. When the type of cake has been identified, work to eliminate the problem can be initiated in a predictable, organized approach. Once the cause for cake formation is understood an assessment of the probability of success can be made with greater confidence. Not all caking problems can be eliminated under all conditions. The classical principles underlying cake formation are taught in this book in a simplified manner, requiring a very limited knowledge of mathematics, chemistry, and physics to understand the basic concepts. The goal is to give the reader a knowledge of the basic science governing cake formation, while offering a standardized procedure to determine the critical factors involved in any caking problem. This book was written for applied scientists with pragmatic, profit-stealing caking problems. An attempt has been made to include concepts with direct applications, while avoiding the temptation to treat each subject in detail. This means that a number of important subjects must be handled incompletely, but to cover them in the manner they deserve would be much more ambitious than the intended scope of this book. This constitutes the author's apology for this deficiency and no additional mention will be made of this point.

Edward J. Griffith

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CHAPTER ONE

Introduction

For any product to survive in an environment of global competition, a quality product at a competitive price is imperative. Any industry producing powdered solids, whether they are foods, detergents, coal, ceramics, cements, explosives, dyes, pigments, fertilizers, or chemicals, cannot consider their products as Quality Products if these products arrive at a customer's home, plant, or work site caked and lumped to the degree that the product is not ready for immediate use. When schedules are interrupted or the product must be disposed of rather than used, a customer cannot be pleased. Disposal can be a very expensive if a large quantity of even a safe substance must be scrapped. It may be less expensive to send the product back to the manufacturer to be reworked. In all cases the aggravation caused by products that do not perform as expected is enough to kill a product which might otherwise perform in an outstanding manner.

Few quality properties of a powdered product are any more obvious than lumps in a package or box that is expected to be free flowing. It is almost universally true that lumped materials will be considered poor quality materials and if the customer can find a manufacturer that can supply the same material in a more desirable physical form, he will turn to the other supplier.

The goal throughout this book is to assist the manufacturer of powdered products to produce a quality product at a reasonable cost. The work will be directed toward the chemistry and physics of caking, but packaging and transportation will also be considered. Ideally, a universal solution to all caking and lumping problems is desired but it is unrealistic to believe that this can be accomplished within the restraints imposed on most products. There is small doubt that all caking and lumping problems can be solved if cost is not a factor.

CONCRETUS CHEMISTRY

Most of the history of Earth had already transpired billions of years before mankind made an appearance. Igneous and sedimentary rocks were plentiful and were at least observed, if not understood, by early man. Sedimentary rock formation represents a form of caking where individual particles have cemented together to form a larger coherent body. The outcroppings of these rocks were not unlike the outcroppings that can be observed today.

It is a reasonable assumption that one of mankind's earlier scientific observations was made when he noticed that some particulate matter in his environment would form cakes, especially if they became wet. He probably also noticed that other substances would not form cakes regardless of what he did to them. There was something strangely different about the two kinds of substances. One kind retained his footprint when it dried, while the other retained no imprinted form at all. One kind of substance became hard like stone, while the other kind of substance may have become a dust, blown away by the wind. Modern man is somewhat more advanced than his ancestors but today's knowledge is far from complete and often reasoning is more by association than by fundamental understanding.

The words caking and lumping are poorly descriptive and scientifically unacceptable. Both words have multiple meanings and are in common usage to depict concepts as unrelated as cooking cakes to slang instructions to ignore conditions or events; "Like it or lump it." Even when the subject is clearly understood, it is difficult to forge a consensus as to where boundary conditions should be imposed on definitions. In the context of this book caking or lumping shall be used interchangeably and for the most part shall connote an undesirable condition. A word is borrowed from Latin, *concrescere*, to describe the sticking together of particles and *concretus chemistry* to describe the science, which shall be employed to understand and hopefully prevent the undesired changes from powders to lumps.

This leads to the need for a definition of what is chosen to be called caking. In some treatments, which attempt to be very scientifically rigorous, much ado is made about the differences between adhesion, cohesion, agglomeration, sticking, auto adhesion, flocks, lumps and on and on. It is the desire to be both helpful and informative to the reader but to treat caking and lumping with no great scientific piety. There seldom is elation when a product cakes and from this perspective it is usually a quality of negative value.

Caking is a manifestation of the influence of gravity on solids. In a weightless environment solid particles that were neither sticky nor mechanically entangled should have little tendency to form cakes. Begin with a simple definition of caking.

When two or more macroparticles, each capable of independent translational modes, contact and interact to form an assemblage in which the particles are incapable of independent translations, the particles are defined as caked.

To be completely rigorous the definition should contain several restraining statements with respect to force fields, shearing forces and yield values. As stated it is tacitly implied that the force acting on the system is gravitational and that the system suffers no impacts sufficiently great to rupture the assemblage formed by the macroparticles. In this respect it is desirable that powders and granules emulate liquids as much as is possible, particularly when it is desirable that the particles be placed in motion. It will usually make little difference whether or not a substance is caked if there is no intention of ever having it move or flow.

Controlled caking is often intentionally utilized in processes where it is desired to agglomerate, sinter, prill, pill, nodulize, glue, cement, and so forth, but problems occur when products that should flow freely will not flow from the container in which they are confined, without the application of some external force other than gravity.

Phase transitions are usually involved in the caking of crystalline solids and water is also likely to contribute. But there are numerous examples where caking occurs in completely anhydrous systems. The phase transition may be as simple as the formation of a hydrated salt from an anhydrous salt, if indeed this is simple, or as complex as the dehydration of a hydrated salt or the double melting point of a racemic mixture.

The solubility of a salt, the energy of hydration, the heat of crystallization and hygroscopicity can be important factors. The electrical properties of a crystal can also become involved. Both bridging in conveyors and electrostatic lumping in bottles, cars, and bags can cause problems. Some systems that cake badly are not caked at all in the normal sense but are held by polar interactions, magnetic or electrical. This is to say that there is no physical bridge between particles. Bag set and bottle set can lead to bridged caking, however. Bag set and bottle set will be defined by example. If dense dry ammonium nitrate prills are allowed to stand in a well-sealed bottle for an hour or more, a cake will form in the bottle. The cake can be broken up by shaking the bottle until the prills are free flowing. If the bottle is allowed to sit quiescently, the lump will reform. The cycle can be repeated endlessly with no degradation of the prills. This behavior is caused by an electrostatic charge on the crystals or prills.

Amorphous solids can have yield values low enough to allow the substances to flow under gravitational force. This kind of caking occurs when granules of tars or waxes become warm enough to flow together. A commonly encounter manifestation of this type of caking occurs when gelatin capsules, of the type used to contain vitamins, stick together from one day to the next. Usually the cake will disintegrate when the bottle is bumped sharply, but one capsule stuck to the bottom of the bottle may, at times, be very difficult to dislodge.

Mechanical caking can range from systems as simple as coat hangers or fish hooks to the entanglement of cotton in bales. Some very interesting studies that deal with the formation of knots have been published [1]. It has been shown that there is a general mathematical polynomial to describe knots. Although detailed descriptions of entanglements are not possible at this time, much progress has been made in relating factors as bulk density and aspect ratio [2]. Aspect ratio is the length of a particle divided by its diameter. It is not unlikely that at some future date it will be possible to describe mechanical caking mathematically. Velcro is a useful two-dimensional example of mechanical caking.

Because modern society continues to be plagued with caking problems, many scientific papers have been published which deal with specific problems of caking. Some excellent treatises have been written which offer detailed coverage of the science of particle interactions and the physics of long range and short range forces. *Adhesion of Dust and Powder* by Anatolii Zimon is a classic [3]. An understanding of these works is imperative for an in-depth knowledge of the interaction of particles and the media in which they are contained, but the technicians faced with their own unique caking problems may have no place to turn for help. It is a prime objective of this book to offer a starting place for those faced with caking problems, but who have no real desire to master statistical mechanics in order to eliminate a caking problem in a box of soap powder, a sack of sugar or a bag of fertilizer. Some established references on the mechanics of powders have been consulted both for definitions and concepts. *Principles of Powder Mechanics* by Brown and Richards presents many fundamentals of powder technology in an practical and understandable form [4]. The approach presented here is less rigorous but depends heavily on the background information of the established literature.

The science of caking will be approached from a less mathematical basis than is found in the physical treatments. This is to say the subject will be approached more from the view point of the chemist rather than from the view point of the chemical physicist. Alexander Findlay notes in the preface to his classic masterpiece, *The Phase Rule and Its Applications,* "Although we are indebted to the late Professor Willard Gibbs for the first enunciation of the Phase Rule, it was not till 1887 that its practical applicability to the study of Chemical Equilibria was made apparent. In that year Roozenboom disclosed the great generalization, which for upwards to ten years had remained hidden and unknown save to a very few, by stripping from it the garb of abstract Mathematics in which it had been clothed by its first discover" [5]. Every effort will be made to avoid this pitfall. Solubility, vapor pressure, hydration, phase transitions, thermal history, crystal properties and electrical behavior will be covered in detail and though scientific in their content they are more easily visualized than concepts presented as abstract mathematical equations. This is in no way intended to imply that a physical approach is not vital. It is! The reader is encouraged to read some of the in-depth treatments listed with the references.

Many industries have been plagued with caking problems for decades and one sure criterion of a quality product is whether or not it cakes under normal use conditions. If a product cakes, it is a reasonably good indication that the formulators did not have a clear grasp of the physical chemistry necessary to control the physical properties of their products. To be sure, environmental issues have made superior powdered products almost impossible to manufacture but satisfactory products can be manufactured, particularly when there is no longer a truly superior bench mark by which the customer can judge performance [6]. It can be stated with reasonable certainty that no other product on a grocer's shelves has had more scientific research expended upon it than the detergents. Fortunately, the formulated products have behaved well enough in their boxes that only a small fraction of the research has been spent on caking problems.

The institutional and industrial segments of the detergent industry, are intentionally casting powdered detergents into blocks. This yields a product that is easily dispersed in automatic equipment and avoids the problems associated with caking. The detergents used in the industrial and institutional markets are very similar to the detergents used in households in years gone by.

The problems associated with lumping and caking are so universal, and in some industries so commonplace, that they are accepted as a part of the business. Some products are cast in drums when manufactured and giant "can openers" are used to remove the drums from the products. As a result of these circumstances, it is difficult to obtain records of the cost of caking. In years passed, the fertilizer industry treated caking as a part of farming. A farmer expected to beat a bag of fertilizer with a sledge hammer before dispersing it on his soil. Parts of the industry intentionally caked the products in bins during manufacture and depended on milling the product before bagging it [7]. This allowed hot products to cool through transitions or damp products to hydrate fully before the product was milled. The storage of a product before milling was usually referred to as aging the product. Although aging was usually successful, it was expensive because a backlog of product was held in inventory for hours or days before it could be milled.

Milling could include blasting the solid blocks with dynamite in order to break it into particles that could be milled with conventional milling equipment. In some cases the fertilizer industry has led the way to liquids rather than solids and in the case of anhydrous ammonia even gases have been used. It is often much easier to distribute a liquid than it is a solid but care must be exercised by the consumer to be certain that the cost performance of liquids is at least as good as the cost of performance of solid fertilizers. In this case performance is usually measured by the yield per acre and grade of the harvest.

For many years ammonium nitrate has been a part of both the fertilizer and the munitions and blasting industries. Ammonium nitrate caking has been an example of most of the possible problems a granular or prilled product can cause when caking occurs. Sometimes when ammonium nitrate was a part of a cake, disastrous results were obtained when the cake was blasted in an effort to reduce the cake to lumps that could be milled. The caking of ammonium nitrate will be given considerably more attention in the chapter dealing with typical examples.

THE COST OF CAKING IN TIME AND MONEY

A part of the difficulty in estimating the time and money that is lost each year as a result of caked products is that the indirect expense is probably as great as the product loss itself. Production schedules are missed. Products are returned to the manufacturer to be either reworked or discarded with transportation cost and paper work on both ends of the transaction. As previously mentioned, it is often difficult to find economical means of disposing of a large quantity of a commodity and the substance may have to be reworked, regardless of cost. In this way a substance that would otherwise be regarded as waste can be spread over an entire nation or the globe to perform a useful service, while it is disposed of in a more acceptable manner. In this way we may literally eat our own waste as an acceptable way of disposing of it but at a very high price to the public who ultimately pays this bill.

When all factors are considered, the cost of unproductive cake products is probably in excess of one billion dollars per year in the United States alone. At the time of this writing there was a trainload of finished powder that was caked in its railroad shipping cars. It had been shipped from the northeastern United States to Mexico and back with no customer desiring a product that cannot be unloaded by the more or less standard methods. More time and money will be spent on the inferior product than a new product meeting specifications should cost. Only one product in the plant of a major producer of food-grade products was estimated to have cost the company over one million dollars last year, as a result of caking problems. Bauder reports that in a plant producing a powdered gravy food product that twenty-five percent of the downtime of the plant's packaging line was attributable to caked product [8].

Help was requested from the Stanford Research Institute and several agencies of the United States Government in an effort to arrive at a number that was something more than a guess as to how much it cost the people of the United States each year because of product caking. After a considerable effort it was concluded that an authentic value could not be calculated. Rather than leave the question completely voided, a value will be calculated based on some assumptions that are believed to be conservative.

The first assumption to be used in estimating the cost of caked products in both direct and hidden cost is, 0.5% of the cost of all finished powders and granules is directly related to caking problems. For typical systems the following values can be calculated.

The data in the following table are presented to point out the magnitude of the problem and are not intended to be anything more

TABLE 1

Industry	*Estimated Value of Goods** *(in billions of dollars)*	*Cost of Caked Goods (in millions of dollars)*
Drugs, soaps, etc.	53.9	269
Fertilizer	8.9	44
Inorganic Chemicals	68.7	344
Stone, clay, glass	55.0	275
Sugar and salt	4.2	21
Total value 1985	190.7 billion	953 million

*Estimates based on data from Statistical Abstracts of The United States 1986 than estimates. The difficulty in obtaining reliable data does bring attention to the need for the collection of data of this type by some reliable organization. Perhaps the United States Department of Commerce would be an appropriate organization. With the collection of data, it would become evident that either more work should be committed to understanding the caking phenomenon or that the problem does not consume a sufficient portion of the national resources to make it worthy of the research required to solve the problems of industry and the citizens of the world.

Large industries have been established to manufacture equipment exclusively designed to handle powdered or granular solids. Rail cars and trucks are but the beginning of the equipment list. Belt drives, shovels, air conveyors, or screw conveyers are in common use, as well as a variety of shakers and pneumatic or electrical hammers. Some very large equipment is capable of emptying a railroad freight car or a truck by turning the car on its side and dumping its contents into a suitable bin. Depending upon the type of storage, if any, to which a product will be subjected, it may be placed in a silo or even bagged. If bagged and placed in a warehouse, any number of circumstances can influence the bag during storage. The season can play a very important role in the history of the product. In the spring and summer months, the temperature of a stored product is likely to experience wide swings from day to night, particularly if the product is stored on the side of a warehouse that receives the afternoon sunshine. In the spring and summer months the partial pressure of water vapor in the air surrounding the product is likely to be much higher. Products that behave very well during winter months may give many problems as the conditions change in the spring. Problems that occur as a result of static electricity may worsen in cold dry conditions. If the product contains any free water or hydrates which decompose at relatively low temperatures, water will migrate from the hot side of a container toward the cooler parts of the container where it is likely to hydrate lesser hydrated salts or anhydrous crystals. In either event a phase transition has occurred both when the hydrate decomposed and when the new hydrate formed.

If a product has been stored in bags, other variables become active. The surface area of the product is usually increased many times over the surface-to-volume ratio of bulked materials. This means that heat transfer to the surroundings will change. The tendency of water to migrate will change. The area to absorb water from the atmosphere will increase if the bags are not well sealed against moisture. Most bagged products are stored in stacks on movable platforms (dollies). The location of a bag in a stack must be considered. Bags placed at the bottom of a stack may be subjected to tons of