Eliminating caking problems

Test methods provide guidance on storage methods

Dr. Jerry R. Johanson
Brayton O. Paul, P.E., Senior Technical Editor

One of the most exasperating problems in chemical plant operations is caking.

Often occurring when bulk solids and powders in outdoor storage vessels experience temperature cycles and are subsequently hardened by crystal growth between particles, caking can turn many dry chemicals into hard, solid masses.

This can often cause damage to the vessel itself and, at the very least, requires the time-consuming and sometimes dangerous act of removing the mass from the vessel.

In the past, plant personnel have relied on hard-earned experience to determine a solid's propensity for caking.

However, testing can determine the caking potential of a bulk solid, eliminating potential vessel damage and enabling the determination to be made in significantly less time than empirical evidence.

Caking mechanisms

Caking, or the agglomeration of smaller particles into large chunks of a solid mass, is the primary cause of time-increased bulk strength with water-soluble solids.

For this to happen. both a liquid (usually water) and a liquid-soluble solid must be present. When only minute amounts of liquid are present or with slowly dissolving s solids such as adipic acid, it also may be necessary to have superfine particles present. These superfines readily dissolve in the limited available liquid, making the glue that binds the larger particles together.

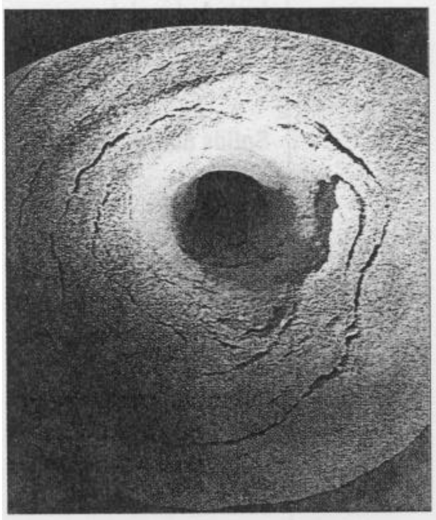
With easily dissolved crystals such as sugar or table salt. the presence of fines is not essential because the larger crystals will quickly dissolve.

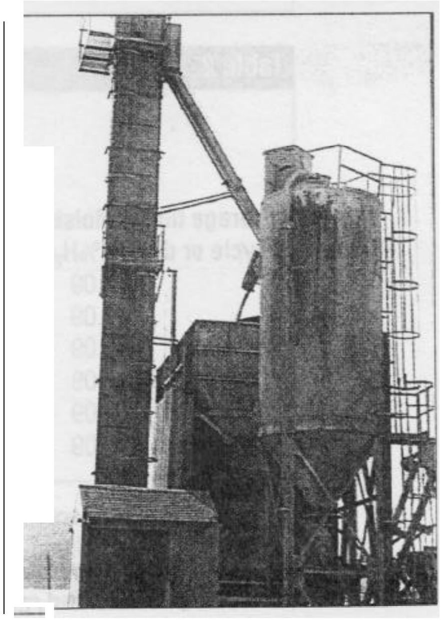
The final element necessary for this mechanism is a means of creating supersaturated solutions at particle surfaces. In bulk solids, this is usually caused by moisture migration in the solids. Subequilibrium and non-uniform moisture contents in a bulk solid can cause moisture migration.

For example, if a soluble solid is sprayed to keep dust down as it enters a storage bin, the liquid will generally concentrate in the fines. This is good for dust removal. However, if the total liquid content is below the equilibrium moisture, the liquid in the fines will migrate to the drier solids and could leave behind supersaturated areas ready for crystallization and strength gains. Because this moisture migration occurs only once, the gain in strength is usually limited.

A more severe strength gain occurs when repeated thermal gradients cause liquid migration throughout the bulk solid. During bulk solids shipment and outside storage, solids are usually subjected to day/night temperature swings. Walls of outside storage bins, railcars or trucks can easily vary in temperature from 40°F at night to 110°F during the day when the sun warms the walls. A surge bin next to a thermal process may be subject to both process temperature variations and process cycle times. In a continuous process, severe temperature variations may occur only during downtime or during upset conditions.

Typical laboratory tests are subject to room day/night temperature fluctuations. However. if the test apparatus is located directly under an air conditioning/heating inlet. temperature fluctuations may be much more rapid as the systems turn on and off several times during the day. All of these temperature fluctuations may





Top: Ratholing is the result of severe caking during storage. Temperature cycles during storage may produce this caking problem with low moisture-soluble solids.

Bottom: Severe caking problems affect silo storage of soluble solids.

Table

Factor	Effect
Moisture content	Low moistures are more likely to cause problems. High moistures may dissolve recrystallized solids and prevent strength gain.
Moisture distribution	Poorly distributed moisture may cause moisture migration through the solids and provide areas for recrystallization and strength gain. This is especially important when the moisture content is below the equilibrium moisture.
Presence of superfines	This may be especially important when the water in a solid is very slight (less than 1%). In this case, recrystallization depends on superfines dissolving in minute quantities of water.
Included moisture	Some materials have included moisture in the particles or crystals. This can be a source of moisture for strength gain, especially with temperature fluctuations.
Solids dissolution rates	Solids that dissolve rapidly generally do not need superfines to cause a severe strength gain. Slowly dissolving solids are more likely to require the presence of superfines. Many solids have a significant increase in dissolution rates with increased temperature. This causes a strength gain as a function of absolute temperature as well as temperature fluctuations.
Crystal growth rate	In general, crystals that grow slowly tend to be stronger than those grown quickly. This results in larger strength gains in long temperature cycles and smaller strength gains with short temperature cycles.

Table 2.

		Rathole index (RI), 2-hr cycle from 91°F to 114°F		Rathole index (RI), day at room temperature from 65°F to 75°F	
Storage time (cycle or day)	Moisture before ($\%H_20$)	RI (ft)	$\%H_20$ after	(ft)	$\%H_20$ after
1	0.09	65	0.05	2.0	0.10
	0.09	68	0.05	2.4	0.08
2	0.09	62	0.04	0.8	0.03
	0.09	71	0.10	1.1	0.07
3	0.09	64	0.03	0.6	0.05
	0.09	66	0.06	0.9	0.05

Table 1. Factors affecting long-term strength of soluble bulk solids.

Table 2. Ratholing indices for granulated sugar with moisture added, tested at **room temperature and cycles from 91°F to 114°F.**

influence the time strength of bulk solids and contribute to the variations measured in the laboratory and observed in a solids handling operation (Table 1).

Tests to determine caking

Caking is measured by determining the shear strength of the assemblage of granular solids after they have been subjected to temperature cycles while standing under consolidation pressure for the prescribed time.

The sample of granular solids is confined in a cylinder under a consolidation pressure equal to a IO-ft head of solids. After exposing the sample to temperature variations, the consolidation pressure is removed from the cylindrical sample and a portion of the bottom support is removed, leaving the caked solids suspended on a ledge. A force is then applied that shears the cake. The magnitude of caking is determined by this force and is interpreted as the size of the rathole (an empty vertical pipe that is made from the caked solids) that will cause such caked solids to collapse as they are removed from the pipe.

The caking test results in this article were derived using an uniaxial shear tester that directly measures the strength of a sample with a single test on one consistent sample. This is crucial to measuring caking effects because slight changes in moisture content from one sample to another can produce significantly different strength values.

If more than one sample is required to measure strength, the data are very difficult to interpret.

Test results

The following test results illustrate that temperature cycles as small as 15°F can cause severe caking, and the addition of tines to coarse granular solids may severely increase caking strength in some cases.

The results also show that with some materials. the caking effects can be duplicated with relatively short, 2-hr temperature cycles. However, these short-term cycles do not always produce the same caking severity that 24-hr cycles produce.

Finally. the test data show that keeping the pneumatic conveying air dry may eliminate caking completely.

This article contains results for sugar, table salt, a detergent additive and adipic acid. Each material illustrates a different aspect of the strength gain mechanism.

Table 2 shows test results for granular sugar with less than 0.1% moisture. The 2-hr cycling between 91°F and 114°F caused a severe strength gain after one cycle. Subsequent cycles did not show any additional strength gain. The dual numbers on one test are repeats of the same test. The data are very reproducible.

The same sugar test subject to relatively constant room temperature conditions showed no significant strength gain after three days, because the room temperature fluctuations were not large enough to activate the recrystallization process.

The practical conclusion from these tests is that sugar stored in an outside bin will cake and show a significant strength gain. However, in a controlled-temperature environment, the slightly moist sugar will show little tendency to cake. The tests also show the effectiveness of short-term temperature cycles in causing caking.

Table 3 shows results using granulated sugar with 3% powdered sugar added. Except for some scatter (likely caused by fines segregation). the results are essentially the same as the granulated sugar results in Table 2. The slightly reduced strength results also suggest that the fine sugar may have picked up some of the moisture in agglomeration, making it unavailable for cementing larger granules together.

The practical conclusions are the same as the granulated sugar results except that adding superfines may decrease caking slightly

Table 4 shows test results for table salt exposed to high-humidity air for a few minutes to allow a moisture content increase of about 0.6%. This roughly sim-

3. [redacted]

Storage time (cycle or day)	Moisture before ($\%H_2O$)	Rathole index (RI), 2-hr cycle from 91°F to 114°F: RI (ft)	$\%H_2O$ after	Rathole index (RI), day at room temperature from 65°F to 75°F: RI (ft)	$\%H_2O$ after
1	0.08	52	0.03	0.6	0.08
	0.08	56	0.05	1.0	0.08
3	0.08	38	0.03	1.9	0.04
	0.08	59	0.07	2.5	0.04

Ratholing indices for granulated sugar mixed with 3% powdered sugar and moisture added, tested at room temperature and cycles from 91 °F to 114°F.

Table 4.

Storage time (cycle or day)	Moisture before ($\%H_2O$)	Rathole index (RI), 2-hr cycle from 91°F to 106°F: RI (ft)	$\%H_2O$ after	24-hr cycle from 91°F to 106°F: RI (ft)	$\%H_2O$ after	Constant temperature at 90°F: RI (ft)	$\%H_2O$ after
0	1.13					2	1.05
	1.13					2	1.03
0.0833	0.49					9	0.35
2hr	0.49					9	0.29
0.167	0.54			-	-	[illegible]	[illegible]
4 hr	0.54			-	-	7	0.42
1	0.49	19	0.36	-	-	-	-
	0.57	la	0.40	-	-	-	-
	0.57	52	0.38	-	-	-	-
	0.54			85	.44	16.6	0.44
	0.54			163	0.41	16.6	0.44
2	0.49	39	0.42	-	-	33	0.53
	0.49	44	0.36	-	-	38	0.41
	0.55			327	0.84	-	-
	0.55			333	0.70	-	-
3	0.61	97	0.34	214	0.86	55	0.45
	0.61	98	0.37	384	1.23	55	0.45
9	0.55	219	0.37	571	1.34	41	0.54
	0.55	259	0.33	1120	1.27	41	0.54

Ratholing indices for table salt exposed to 116°F air saturated with water, tesrea au remperarure cycles from 91°F to 106°F and at a steady temperature of 90°F

Table 5.

Material	Ratholing index (RI), ft	Flowrate index (FRI), lb/min
Large particles (≅14 mesh)	3	2,200
Same with 25% of -200 mesh added	17	1

Ratholing and flowrate indices of monomer, tested at four 2-hr temperature cycles from 91 °F to 114°F.

ulates the moisture gain if the salt were conveyed pneumatically with warm, moist air. Results showed that with a constant temperature, salt gains a maximum strength after about one and a half days of storage. One-third of that gain occurs in the first 2 hr of storage.

This strength gain is likely caused by moisture redistribution in the sample to obtain an equilibrium condition. Once equilibrium is obtained, the strength remains constant.

The cyclic testing shows a linear strength increase with the number of cycles. The dramatic difference between the 2-hr and 24-hr cycles is an example of crystal growth rate effects on strength gain.

There is roughly a factor of five between the strength from the short 2-hr cycles versus the 24-hr cycles.

The practical conclusion is that salt, if it fluctuates in temperature between 91°F to 106°F in a few days, will be extremely difficult to remove from a bin and will get progressively worse. This strongly suggests keeping the salt dry and not conveying it in moist air. This conclusion is the same for both the 2-hr cycles and the 24-hr cycles.

Cyclic testing was used to simulate several weeks of storage of a detergent additive. The as-received granular detergent additive showed no strength after 44 cycles. However, after exposing the additive to warm, humid air to simulate pneumatic conveying, the strength is very large after 44 cycles.

The results show that if pneumatic conveying air is not kept dry, there will be severe handling problems with the additive after a few weeks of storage.

The acceptable conveying air moisture level can be established by running cyclic strength tests after preconditioning the additive at various conveying air moisture levels.

In conclusion

Temperature cycles during storage may produce severe caking problems with low moisture-soluble solids.

There is some additional research required to choose the cycle time for a given bulk solid that best duplicates longer time effects.

Case study

Adipic acid, which is used to make nylon, is frequently transported by railcar.

Because it readily cakes, railcar unloading is sometimes difficult. Some adipic acid discharges in 5 hr, while other shipments require 24 hr or longer to unload because of severe caking problems that require poking, prodding, pounding, and even air lances to break up lumps and initiate flow.

The cake-type adipic acid was easily identified by measuring the ratholing index (RI) for the various samples when they were subjected to temperature cycles, Those with a RI greater than five showed increased unloading times. A RI greater than 15 caused extreme unloading difficulties.

Table 5 shows typical results of adipic acid with and without fines. Note that the RI changes from 3 to 17 with fines addition. The flowrate index (FRI), which is a combination of permeability and compressibility, decreased from 2,200 to 1 with the fines addition. A low FRI decreases as a high fines content increases.

Tracing the various samples back through the production line indicated that the adipic acid that unloaded easily was often associated with a production line that had additional cyclone fines separators and consequently contained slightly less -200-mesh particles.

The difficult-to-unload adipic acid samples always came from the line with only one cyclone fines separator and, consequently, contained more -200-mesh particles. The solution in this case was to install another cyclone fines separator.

However, the presented methods yield useful, practical results that provide excellent engineering guidance.

■ To receive the papers "Characterizing Dry Particulate Solids for Systems Design," presented at the International Fine Particle Research Institute Annual Meeting, Pasadena, CA, June 1993, and "Toward a Common Goal," from the British directory, "Who's Who in Bulk Handling Yearbook," 1995-JR Johanson Inc., San Luis Obispo, CA. CIRCLE 519

Dr. Jerry R. Johnnson is the CEO of JR Johnnson Inc., San Luis Obispo, CA.