About the Flowing Process
Submitted by George Wells

A lot has been written about the production of flow blue and mulberry china, but when potters and collectors attempt to explain the actual science of such processes, misinformation is often the result. In my opinion, the question of how flow blue and mulberry decorations were made to flow has never been adequately answered. While a fairly good selection of accounts describing exactly <u>what</u> was done may be found, particularly little is offered in explanation of <u>why</u> the apparently magical flow-producing steps worked. Although the potter's "art" or experience influenced his or her choice of ingredients and firing temperatures- and with fairly accurate results- the all-important flow-determining events were happening at the molecular level, about which the potters of the mid-19th century were essentially ignorant. When those potters reached the "retrospective" stage of their careers and wrote their memoirs, they either relied on the prevailing "wisdom" (which was often incorrect) or simply invented the science parts altogether. Some of the more recent authors on the subject (often those whose most legitimate claim to authority lies in the number of photographs they can obtain) compound the problem by tending to make a habit of paraphrasing previously published misinformation. I have studied much of what has appeared in print on the subject of "flowing", and this monograph is my attempt to make at least a bit of sense of this one aspect of the production of flow blue and mulberry china.

Petra Williams mentioned in her first volume on the subject that, in general, cobalt oxide decorations "blurred a bit in the glazing period" and that it was discovered that the blue could be made to flow more copiously "by instilling lime or chloride of ammonia in the sagger while glazing." Other authors have added to the list of "instilled" chemicals, and have pointed out that they were known as "flow podders" or "flow powders" by the potters who used them. If considered in the correct order and context, these select phrases are accurate, but leave curious readers wondering whether flow powders were truly the responsible agents of flow, and if so, "How did they work?" The answers are a matter of glass chemistry, which, in turn, is nothing more than a special case of simple solution chemistry.

Pottery glazes are glasses which have characteristics that make them suitable for use as a surface coating for pottery. Even "salt-glaze", which is produced by throwing common table salt into the hot kiln, is a glass formed when sodium vapor from the salt combines with the silica on the surface of the pottery. Now, an interesting fact about glass (and thus glaze) is that even at room temperature, it is a super-cooled liquid rather than a true solid- it has no crystalline structure. Most mineral substances crystallize when they cool to a temperature below their melting point, but glass does not. Once melted together, the components that form a glass exist as an amorphous (randomly-structured) liquid that never entirely solidifies, regardless of temperature. Many of the properties of glass depend upon this phenomenon. Even at room temperature, the components of glass continue to behave much like the components in a vessel of water into which a variety of other materials are dissolved. They simply do so at an exceedingly slow rate. It is at the hotter kiln temperatures, however, when glaze becomes particularly molten, that most of what we are interested in takes place.

In the early production of cobalt blue-decorated wares (note that we are NOT talking about flow blue here) cobalt oxide decorations were placed on pottery by a variety of well-described techniques: transfer, brushstroke, etc.. The decorated pieces were then gently heated to evaporate excess moisture, after which the piece would be dipped into a slurry of glaze. The "glost" firing would then burn off the pigment's medium (greasy, waxy stuff) well before the siliceous components of the glaze fused. During the glost firing, while the glaze was molten (during the "soak" at maximum temperature), some of the cobalt oxide would manage to dissolve into the glaze, producing a lovely, deep cobalt blue color in the process. Such pottery was not, however, significantly "flown", as we tend to use the word.

Cobalt oxide dissolves in molten glaze much like table salt dissolves in water, with the cobalt oxide dissociating into its component ions, which then bond to other suitable components of the hot liquid glaze. The cobalt ions specifically associate with silicate ions and the resulting cobalt silicate is a compound that has an extraordinary capacity for absorbing all visible light <u>except</u> than that which our eyes perceive as being deep blue in color. While quite a lot of salt can dissolve into a given volume of warm water, the solubility of cobalt oxide in glass and/or glaze seems to be limited to approximately 2% by weight. (This figure shows up in numerous formulations and apparently reflects empirically determined practical limitations rather than a theoretical maximum. Cobalt oxide is simply not nearly as soluble in molten glaze as table salt is in warm water.)

The potters' problem was that while a considerable amount of cobalt oxide could be applied, relatively little of it actually dissolved, and much of what did dissolve just stayed in place, where the intensity of its color approached black. Very little of the blue pigment diffused out into the surrounding glaze sufficiently to produce the flow-like effects we

have come to know and love. This was because, as glasses go, glazes tend to be both particularly thin and particularly viscous by design- thin for the sake of economy and viscous so that they don't run off of the pottery once they melt. Neither of these characteristics proved particularly conducive to color flow. Making the glaze thicker would help a bit, but was materially wasteful (and thick glazes tend to craze more readily than thin ones) and while firing at a higher temperature (or for a longer period of time) led to a bit more flow, doing so was prohibitively expensive <u>and</u> caused the glaze to run.

At some point, a clever potter figured out that if, before the glaze was fired, certain chemicals were tossed into the sagger (one of the ceramic "bread-boxes" that were used to protect the china from the furnace's internal environment) the under-the-glaze cobalt decorations (and some others, as well) could be made to flow MUCH MORE.
The advantage of enhanced flow was immediately appreciated: the cobalt oxide was expensive, and relatively less of it would be needed to produce a given effect if more of it could be induced to dissolve and diffuse into the glaze. This idea came directly from salt-glazing, which was a similar, chemical-tossing process which had been in widespread use through much of the 18th century. But why exactly did it work?

Well, first of all, salt-glazing works because at the firing temperature, sodium chloride decomposes into sodium and chlorine vapors. The sodium vapors react readily with the silica on the pottery's surface to form sodium silicate- a glass - thus the term "salt glaze." The properties of salt glazes are such that they are usually quite thin and not particularly smooth, but they proved to be very well suited for covering earthenware – particularly stoneware – some of which was decorated with cobalt oxide. Salt-glazed jugs of the mid-1700s can be found with cobalt blue decorations flowing all over the place! There are numerous references to "flow'd stoneware" that are contemporary to their production in the mid- to late-1700's. (See survey of household inventories, Plymouth, Massachusetts, 1784 & 1789, "White Salt-Glazed Stoneware of the British Isles," Edwards and Hanson, p. 165.) The terms "flow'd," "flowing" and "flowing blue" were in use well before 1800. The "flowing" process was also applied to some cobalt blue-decorated pearlware made in the 1780 – 1800 period. (See "Painted in Blue," Lois Roberts p.105 for an example.)

By the 1800's, the idiosyncrasies of salt glazing were well known to the Staffordshire potters, and in particular the effect it had on cobalt oxide decorations was well understood. It was only a matter of time before someone seriously undertook to fire some cobalt-decorated <u>transferware</u> in a sagger that was either intentionally charged with salt, resulting in the recovery of a sagger full of flown transferware china! It was be no accident that sodium chloride (salt) was one of the first and most common of the "flow powders", and that the powders were added in a manner similar to the addition of salt in salt-glazing, at least until the next level of innovation was reached, in which the flow powders were added directly to the glaze.

In general, substances which are soluble in a liquid will, upon contact with the liquid, begin to dissolve into it. The amount that can dissolve depends on the temperature of the materials as well as the degree of affinity they have for each other. In the case of glaze, the temperature is particularly important because if the "liquid" is too cool, it will be so viscous (the opposite of free-flowing) that the dissolving material (cobalt oxide) cannot readily disperse into it, and the local concentration of the pigment will quickly reach its limit of solubility. The affinity between the two materials is important because if they cannot tolerate each other at the molecular level, very little co-mingling (dissolving) will occur, regardless of the temperature.

Once dissolved, the cobalt pigment (re-associated as cobalt silicate) is compelled to disperse within the glaze by the "Brownian motion" (a kind of wiggling) of the solution molecules. Locally, as some cobalt disperses, more can go into solution. In an "ideal" solution, it is this Brownian motion, coupled with entropy (the need for a system to reach the state in which its potential energy is at its minimum) that would drive the solution components <u>toward</u> an equilibrium distribution in which all components are equally dispersed... but this isn't an "ideal" solution. Fortunately, time limitations prevent our flown china from ever reaching a uniformly blue end-point. More importantly, It is the viscosity of the molten glaze and the relative amount of "clearance" within the molecular matrix that determines how far the pigments travel within the glaze in a given amount of time. It is this resistance to motion that is overcome by the absorption of flow powder vapors.

Instead of raising the temperature of the kiln or increasing the firing time (both of which would have been very expensive) the potter was able to change the chemical properties of the glaze by adding to the sagger one or more of a variety of salts which would vaporize at the firing temperature. The vapors produced by these salts were more or less contained, if only temporarily, within the sagger. (The saggers were not air-tight- they would have exploded upon

heating if they were.) And during their containment, some of these vapors dissolved into the molten glaze, changing its chemical composition and thus either its viscosity or its affinity for the dissolving pigment.

THE ROLE OF ALKALINE METAL IONS:
Alkaline flow powders (those which contribute sodium, potassium or other similar alkaline metal ions upon thermal volatilization) have a very pronounced ability to lower the viscosity of the molten glaze, and thus the rate at which dissolved cobalt (or other pigment ions) can move around. Alkaline earth compounds (those which contribute calcium, magnesium or other similar alkaline earth metal ions) have a similar effect, although the viscosity of their resulting modified glazes will be more temperature-dependent than the corresponding alkaline-modified glazes. Essentially, any "flow powder" which produces basic (alkaline or alkaline earth) flux vapors which are able to dissolve into the molten glaze will at least somewhat reduce the viscosity of the glaze, and thus the mobility of any dissolved cobalt. The more these vapors dissolve into the glaze, the more the glaze properties change in a way that allows the cobalt to flow more freely. A benefit of using flow powders which reduced glaze viscosity was that they lowered the temperature at which the desired viscosity of the glaze would be reached, so that the potter was able to fire his glazed wares at either a somewhat lower temperature or for a shorter period of time. (The viscosity couldn't be lowered too much, however, or the glaze would run.)

Lead compounds have also been used as flow powders. When lead compounds volatilize in a sagger, some of the resulting lead vapor can dissolve into glaze. While the dissolved lead will effect the viscosity of the glaze in the same manner as alkaline fluxes, it may also increase the mean amount of space between glaze molecules, which would in turn effect the rate at which dissolved pigments can disperse. (Gives 'em more room to wiggle around in.)

Complicating the issue of glaze viscosity is the fact that the materials in question do not remain static during their stay at high temperature. The lower-boiling components of the glaze continue to slowly evaporate with time, so that the glaze becomes progressively more viscous. The glaze also bonds (fuses) more thoroughly with the underlying pottery as it slowly dissolves into the ceramic substrate, and this process also alters the glaze's receptivity to pigment flow. It is no wonder that the manufacturers who are attempting to reproduce old flow blue are having a difficult time of it!

THE ROLE OF CHLORIDE IONS:
Other compounds, such as ammonium chloride, lead chloride, sodium chloride, and even hydrochloric acid, upon vaporization, reportedly ("Pottery Decorating", by R. Hainbach) contribute chloride ions to the molten glaze. Upon dissolving into the glaze, the chloride ions preferentially complex with the dissolved cobalt to make a compound which travels more quickly than the cobalt-silicate complex, either by exchanging back and forth between several different intermediate species <u>within</u> the glaze, or by hopping in and out of the vapor phase <u>above</u> the glaze surface. (S. Scholes reports in "Modern Glass Practice" that "chloride ions appear to coordinate with cobalt ions in borosilicate melts…") While it is unclear whether these chloride ions remain in the cooled glaze, or are simply facilitators in the transport of cobalt ions, the empirical evidence strongly suggests that they play a VERY significant role in the flow process. Because the amount of viscosity reduction had to be limited (to prevent glaze run-off), cobalt chloride was likely the most important flow facilitator of all.

No discussion of the flowing process would be complete without mention of the "ghost" images on the reverse sides of many flat flow-china items. When present, these images are always quite blurred, but will usually present themselves in shapes which are recognizably similar to those found in the top-side design. These ghost images are NOT bleed-through images- one need only break open one such piece of china to find that the underlying pottery is totally devoid of cobalt (or mulberry) color. Rather, the ghost images result from a communication of the design from the immediately adjacent piece in a stack of plates or other flat items, either by vapor or effervescent transfer. Some flow blue glazes may be found (most notably on some pieces of CHUSAN by Clementson) that show the unmistakable signs of small bubbles bursting and splashing around the color present in the glaze. (Such pieces, while smooth to the touch, show a mottled color effect, both on the reverse (ghost) and in the background color of the obverse design.) Effervescing was probably caused by carbonates present in the glaze formula, which would, just like Alka Seltzer, release carbon dioxide as the glaze melted. As the carbon dioxide bubbles reached the surface of the glaze, they burst, releasing the gas and splashing any near-by surface. (To feel this effect, hold your face just above a glass of water into which an Alka Seltzer tablet has just been dropped.)

Most flow ghosts do not appear at all mottled, however, and their uniformly diffuse effect strongly suggests a vapor transport origin, probably in the form of the above-mentioned cobalt-chloride. Above the surface of <u>all</u> liquids exists a vapor phase in which the components of the liquid are present. The absence of significant ghosting in non-flown cobalt-

decorated china suggests that by itself, cobalt silicate has an extremely low vapor pressure, and that very little of it moves in the space above the china surface. But when something is added to the system - in the form of flow powder - a new, more volatile species is formed. (Technically, the concentration of the vapors depends in part upon the temperature of the system and the boiling points of the individual components. The melting points of the various cobalt silicides are around 1300 degrees C and the boiling points of those compounds are not even published, while the boiling point of cobalt chloride is a conveniently lower 1049 degrees C (it alone would have a significant vapor pressure at the glaze-firing temperature)- further evidence in support of the cobalt chloride connection.) (The actual cobalt-silicate complexes in the glaze are much more complex than the chlorides, and boiling points for them are also unpublished.) Most importantly, if vapor transport is responsible for ghost images, in which a considerable amount of color has moved over a distance of more than one centimeter, then it is surely also responsible for a very significant amount of the flow on the front of each piece!

Also noteworthy is the occasional occurrence of a plate or platter that exhibits "ghosts" on the reverse side that do not match the front pattern, indicating that not every sagger was filled with items of the same pattern.

There are a variety of other factors that occasionally produced "blurring." Some transferware blurring is simply the result of smearing or rubbing of the transfer during its application. There are also those occasional dramatic pieces upon which the glaze was so thickly applied that both the glaze and the color there-in ran, dripped, slipped or poured according to the influence of gravity. It is sufficient to say that quality control was not in such cases a big issue!

Enough chemistry! (Maybe too much!) The same flow powders that were used to make flow blue also worked on mulberry, for the same reasons. And it didn't take too long (around 1847) for potters to discover that adding the flow powders directly to the glaze was more efficient than putting them into the bottom of the sagger. Then, by the end of the 19th century, tastes had changed, and the extreme flow effects of the 1850's were replaced by more subtle renditions. By then, the desired effects were being accomplished entirely through the manipulation of glaze formulas, and "flow powders" were a thing of the past.

It is important to remember that the use of various flow powders was more or less an arbitrary and very individual thing. No Lawrence Livermore Laboratory report guided the potters. They found by trial and error that many different substances altered the behavior of their glazes, and they used them to obtain the desired effect with varying degrees of success. Even today, there is not a great deal of information in the public domain concerning the solution chemistry of 1300-degree ceramic glazes, owing to the difficulty of analyzing materials at that temperature and the lack of an economic reason to do so. But the flow powders DID work!

Finally, it is important to understand that that "Flowing" was never accidental. Flowing cannot occur simply when kiln temperatures rise above intended levels, excepting that the pottery itself will eventually liquefy. ("Waster" dumps are full of the grotesque consequences of poorly managed kiln temperatures.) The flowing effect was ALWAYS the product of the modification of ceramic process chemistry (intentional or otherwise) to achieve a rare and beautiful phenomenon.