Diffusion of Gaseous Sulfur Dioxide into Corn Grain

S. R. ECKHOFF[1] and M. R. OKOS[2]

ABSTRACT

The diffusion path of gaseous sulfur dioxide into sound yellow dent corn was explored. The iodine-staining procedure used gave qualitative indication that the SO_2 enters primarily through the tip cap in whole intact kernels. The SO_2 enters at the tip cap, moves up through the area between the pericarp and seed coat, and then diffuses into the endosperm. A second pathway up through the germ into the endosperm was also observed. Complete penetration of gaseous SO_2 into the kernel can be achieved in about 2 min. Damage to the pericarp increases the amount of SO_2 taken up by the grain.

Cereal Chem. 66(1):30–33

The diffusion path of gaseous or liquid materials into and through cereal grains is complex, as would be predicted based upon the structure of cereal grains. Although many researchers have modeled diffusion in cereal grains using a spherical diffusion mode (Fan et al 1965, Park and Kyle 1975, Hsu 1984), Cox et al (1944) and Wolf et al (1952) showed that liquids tend preferentially to enter the tip cap or attachment point of the grain, diffuse up through the space between the pericarp and seed coat, and then diffuse into the endosperm of the grain. The seed coat is semipermeable to organic and inorganic materials, allowing water to diffuse through but inhibiting flow of other liquids until structural changes are induced in the seed coat by the diffusing chemical (Beeskow 1924). Gaseous SO_2 has been shown to be effective in controlling microbial growth during the low-temperature drying of corn (Eckhoff et al 1983, 1985; VanCawenberge et al 1979). Microbial infection of grain is not homogeneous, and the location of the organisms depends, among other factors, upon the particular invading organism (Semeniuk 1954). The efficacy of SO_2 treatment could be totally dependent upon the location of the organisms and the ability of the SO_2 to diffuse to those locations. This research was done to determine the diffusion path of gaseous SO_2 into corn grains in order to better understand the diffusion process.

[1]Associate professor, Agricultural Engineering Department, University of Illinois, Urbana 61801.
[2]Professor, Agricultural Engineering Department, Purdue University, West Lafayette, IN 47907.

Procedures

Yellow dent corn, Cargill 1967, was hand-harvested at 30% mc and hand shelled. Samples were stored at −16° C until the test was run. Grains that appeared sound and showed no visible cracks or defects were selected for the experiment.

The grains were exposed to a stream of pure gaseous sulfur dioxide at room temperature for 30, 60, and 120 sec. After treatment, the kernels were removed and sliced into sections using a razor blade. The sliced kernels were dipped into an iodine solution (0.02*N*). Sliced sections were then blotted on tissue to remove excess iodine, and the exposed endosperm and germ were photographed using 35 mm color film. Because iodine reacts with sulfur dioxide to form a colorless compound (Schroeter 1966), the presence of SO_2 in sufficient quantity to react with the iodine taken up by the grain during the dipping results in normal coloring of the kernel. Excess or unreacted iodine reacts with the starch in the kernel to produce a dark colored complex, thus, this staining procedure is a qualitative rather than quantitative measure of the presence of SO_2.

The entire procedure (treating, slicing, dipping in iodine, and photographing) was carried out at timed intervals to insure reproducibility. Ten seconds after the kernel was removed from the gas stream it was dipped into the iodine for 10 sec. The blotting of the excess iodine and positioning took an additional 10 sec, so that the kernels were positioned and ready to be photographed 30 sec after being removed from the gas stream. When multiple kernels were to be photographed at the same time, the length of time from removal from the gas stream to dipping increased to 30 sec and positioning time for the photograph also increased so that total time increased to 1.5–2 min. Photographs of the same kernels taken at different times after removal from the SO_2 gas stream were achieved by shutting the lights off on the photographic stand and

leaving the kernels on the surface.

To help study the entrance point of SO_2 into corn kernels, some kernels were dipped into liquid paraffin 24 hr prior to being exposed to SO_2. The kernels were dipped in approximately one third of their length such that the tip cap was completely covered and approximately one half of the germ face was covered. Also, certain kernels not coated with paraffin were cut with a razor blade deep into the endosperm area of the kernel. The cut was to show the effect of cracked or damaged kernels on the rate of SO_2 sorption.

RESULTS AND DISCUSSION

Figure 1 shows four kernels exposed to pure SO_2 gas for different lengths of time. The exposure times were (from left to right) 120, 60, and 30 sec, or no exposure. There are visible differences between the kernels due to exposure time. The untreated kernel was totally dark as expected, and as exposure time increased, the amount of area lightened by the SO_2 increased until after only 2 min the SO_2 had penetrated well into the kernel. This rapid transfer of pure SO_2 into the grain suggested that long exposure to pure SO_2 may be undesirable and inefficient.

Figure 1 also displays the same four kernels photographed at different times after being removed from the SO_2 gas. Figure 1A was taken 2 min after the iodine was applied, Figure 1B was taken after 5 min, and Figure 1C after 8 min. This series of photographs shows several interesting phenomena. This is demonstrated most clearly in the 60-sec exposure kernel between Figures 1A and 1B. The increased time allows the SO_2 in the kernel to diffuse further, since immediately after removal from the gas stream there are large SO_2 gradients established in the kernel. During the cutting, dipping, and positioning of the kernel for photography, some of the gradient is dissipated as the SO_2 diffuses further into the kernel, vaporizes from the kernel, or reacts with corn constituents. However, some SO_2 gradients remain, and the movement of SO_2

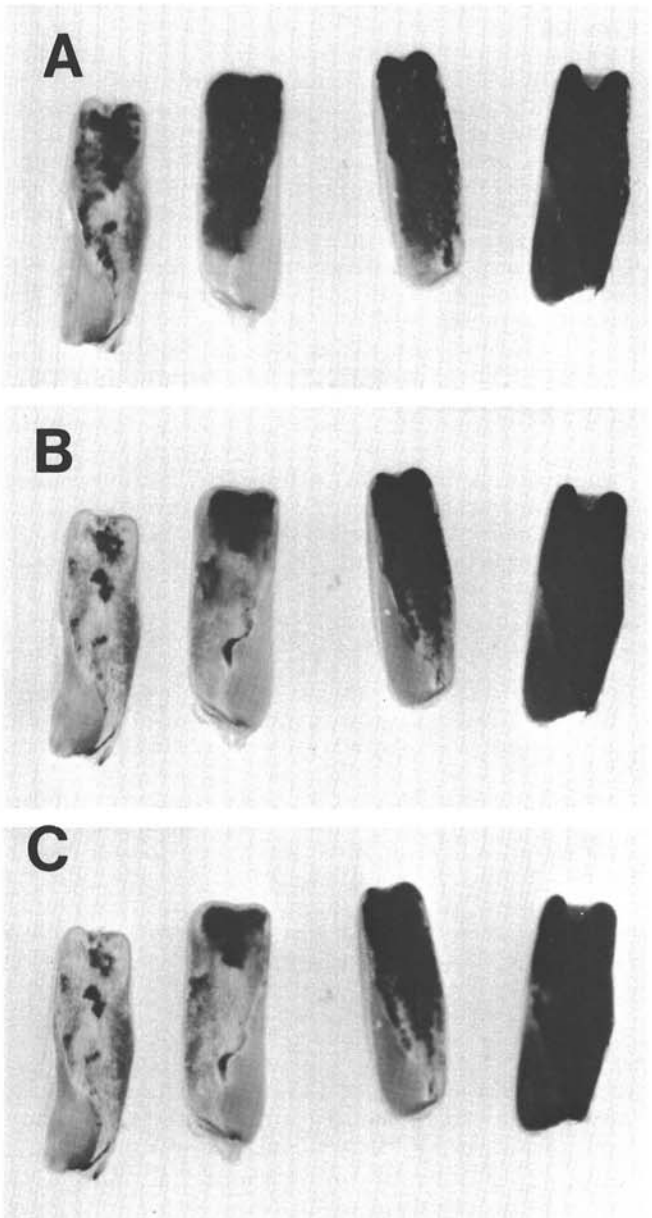

Fig. 1. Kernels exposed to sulfur dioxide for different times (from left to right: 120, 60, and 30 sec exposure, and no exposure) and dipped in iodine to show path of diffusion. Darkened areas indicate low or no sulfur dioxide. **A,** Photo taken 2 min after iodine was applied. **B,** Photo taken 5 min after iodine was applied. **C,** Photo taken 8 min after iodine was applied.

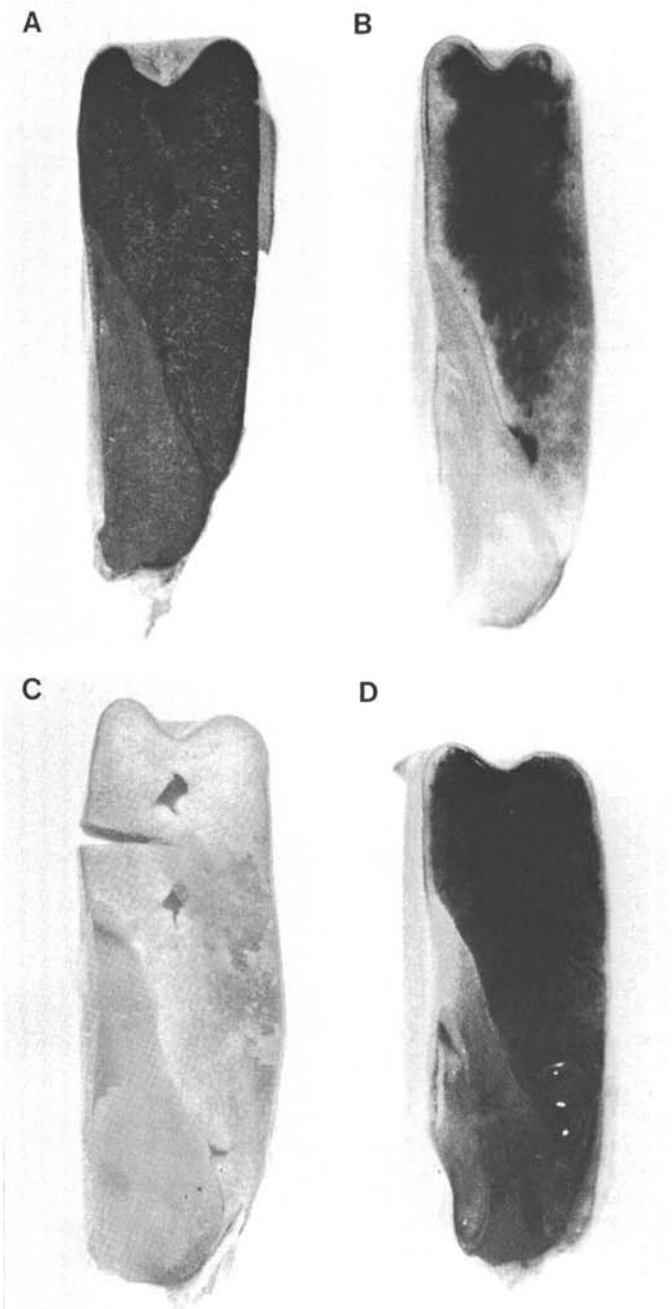

Fig. 2. Penetration of sulfur dioxide into kernels treated to show diffusional barrier or pericarp. Darkened areas indicate low or no sulfur dioxide: **A,** no exposure to sulfur dioxide; **B,** 60-sec exposure; **C,** kernel with deep endosperm cut exposed to sulfur dioxide for 60 sec; and **D,** kernel with tip cap coated with paraffin and exposed to sulfur dioxide for 60 sec.

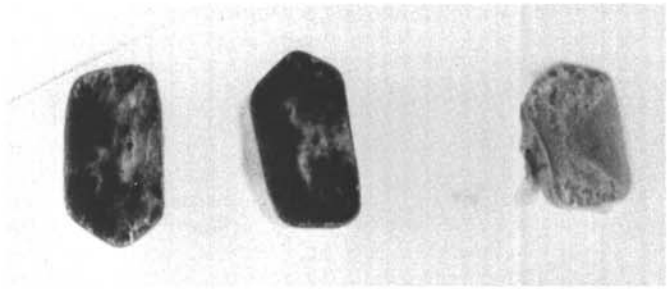

Fig. 3. Cross-sectional cuts of a corn kernel exposed to sulfur dioxide for 60 sec prior to being sliced and stained with iodine. From left to right are sections through the top, through the middle, and through the bottom of the kernel. Photo taken 3 min after iodine was applied.

can be observed. This rate of lightening of the kernel can serve as only a rough qualitative measure of the direction and magnitude of diffusion occurring within the kernel, because the slicing of the kernel has modified gradients within the kernel and may allow for other transfer mechanisms to become important. A secondary reaction with iodine also occurs that causes it to lose its color with time, as can be observed in the untreated kernel. The area near the center of the kernel by the germ lightened with time, as can be seen in Figure 1C. This reaction is considerably slower than the change observed from diffusion.

Figure 1 also shows the pathway that SO_2 follows as it penetrates the kernel. The SO_2 appears to enter primarily through the tip cap, shown by the lack of coloration in the area near the tip cap. As Hoseney et al (1983) showed for popcorn, the pericarp has a higher resistance to diffusion than does the endosperm area. Although popcorn is unusual in experiencing a very short period of high temperature, the data still indicate the relatively higher resistance of the pericarp. SO_2 also appears to diffuse rapidly around the outer area of the endosperm, in agreement with the findings of Cox et al (1944); using liquid demonstrated that sulfurous acid enters the tip cap area and diffuses around to the top of the kernel before starting to penetrate through the aleurone layer into the endosperm. The lightened (reacted) area between the endosperm and the pericarp appears to be larger than could be accounted for by just the area between the seed coat and the pericarp as suggested by Cox. Cox et al (1944), Beeskow (1924), and Freyberg (1931) indicated that seed coats are semipermeable such that water is allowed to pass through but other inorganic or organic substances are denied passage. Our findings indicate that the seed coat offers some increased resistance to gaseous SO_2 transport but does not act as a true semipermeable membrane.

The increased resistance of the seed coat may result from the obvious difference in cell density of the areas. The cross and tube cells are large, loosely packed, thin-walled cells that are designed to facilitate the movement of material through them. The aleurone layer has no large intercellular spaces and thus offers greater resistance to diffusion (Wolf et al 1952). Another factor that helps to explain the apparent semipermeability is the difference in composition and reaction of the two areas. The aleurone layer is high in protein and fat, whereas the bran is relatively low in protein but higher in ash and fiber (Kent 1975). If there is binding or reaction between the diffusing material and the substrate (i.e., the protein or fat), then the apparent diffusivity or movement of the material into the kernel depends upon the rate of reaction relative to the rate of diffusion. In such a case, if the SO_2 rapidly reacts with the aleurone layer, the SO_2 will not appear to be diffusing into the endosperm. Only when all the reaction sites have been used will the SO_2 species appear to diffuse into the endosperm.

To confirm that SO_2 enters the kernel through the tip cap, tip caps were covered with paraffin and exposed to SO_2 for 60 sec. The paraffin acted as a diffusion barrier over the tip cap area. Three kernels exposed to SO_2 for 60 sec are shown in Figure 2 along with an unexposed kernel. Paraffin on the tip cap of the kernel in Figure 2D slowed the uptake of SO_2, as can be seen by comparing Figure 2D with 2B. The dark area in the germ is characteristic of paraffin-covered kernels and is presumably due to the reduced diffusion of SO_2 through the tip cap. Some SO_2 has obviously entered the kernel, as shown by the light areas on the upper germ and on the back side of the endosperm. The pericarp is thinnest over the germ, which would reduce the diffusion resistance at the point. The light area on the back side of the kernel is probably due to a crack in the pericarp.

The kernel in Figure 2C was cut deeply into the endosperm with a razor blade prior to exposure to the SO_2. The cut acted as a second entrance point for the sulfur dioxide, and a 60-sec exposure allowed the SO_2 to permeate the kernel completely. This adds support to the conclusion that the tip cap is the primary entrance (compare Fig. 2B and C).

Not all paraffin-coated kernels showed the same effect as that shown in Figure 2D. Some kernels showed larger areas of lightness, particularly in the endosperm. The darkened lower germ area covered by paraffin was characteristic of all the kernels. But, as shown in Figure 2D, fissures or cracks in the pericarp would increase the amount of SO_2 taken up by the kernel, and it is assumed that such cracks were the cause of the light areas in the endosperm.

Figure 3 shows a kernel exposed to SO_2 for 60 sec and then cross-sectioned. The right section in the photograph is from the lower end of the kernel near the tip cap. As expected, high levels of SO_2 were present as shown by the lack of color. The middle section taken near the top of the germ shows an interesting effect. The light area in the center of the endosperm indicates that the SO_2 had penetrated to that point. It apparently came up into the endosperm by way of the germ. The SO_2 entering via the germ entered initially into the opaque or floury endosperm. This is reasonable because the floury endosperm consists of densely packed polygonal starch granules (Hoseney et al 1983). Most but not all kernels tested showed this pathway into the endosperm via the germ. The SO_2 appears to enter the endosperm by two methods. One is to enter the tip cap, diffuse around the kernel in the area between the pericarp and seed coat, and then diffuse into the endosperm. The second is to diffuse through the germ and enter through the scutellar epithelium between the germ and endosperm. The left section was taken near the top of the kernel. SO_2 has diffused into this section in a manner similar to that shown in the center section, although diffusion through the seed coat is more observable because this section is close to the very top of the kernel.

CONCLUSION

The results indicate that sulfur dioxide enters the intact corn kernel primarily through the tip cap, diffuses around the kernel in the area between the pericarp and the seed coat, and then diffuses through the seed coat into the endosperm. The grain is fully equilibrated with pure SO_2 within 2 min. The seed coat offers resistance to SO_2 diffusion into the endosperm. The results of the test also show a second diffusion path into the endosperm. SO_2 apparently diffused up through the germ and then entered the endosperm and diffused outward toward the seed coat. Not all kernels tested showed this pathway, which may result from a poorly developed or broken scutellar epithelium between the germ and the endosperm.

Kernels with apparent surface cracks or other breaks in the pericarp showed increased sorption of SO_2. The cracks acted as extra entrance points for SO_2. SO_2 sorption appears to be most rapid and complete in the germ. This is beneficial, because many fungal infections occur primarily in the germ. There was no area within the kernel that the SO_2 could not penetrate.

LITERATURE CITED

BEESKOW, H. C. 1924. The Selective Semipermeability of the Seed Coats of Corn. M.S. dissertation. The University of Chicago, Chicago, IL.

COX, M. J., McMasters, M. M., and Hilbert, G. E. 1944. Effect of the sulfurous acid steep in corn wet milling. Cereal Chem. 21:447.

ECKHOFF, S. R., TUITE, J. F., KIRLEIS, A. W., and OKOS, M. R. 1983. Microbial growth inhibition by SO_2 or SO_2 plus NH_3 treatments

during slow drying of corn. Cereal Chem. 60:186.
ECKHOFF, S. R., TUITE, J. F., FOSTER, G. H., ANDERSON, R. A., and OKOS, M. R. 1985. Inhibition of microbial growth during ambient air corn drying using sulfur dioxide. Trans. ASAE 27:907.
FAN, L. T., CHEN, H. C., SHELLENBERGER, J. A., and CHUNG, D. S. 1965. Comparison of the rates of absorption of water by corn kernels with and without dissolved sulfur dioxide. Cereal Chem. 42:385.
FREYBERG, W. 1931. Beitrage zur Kenntnis der physiologie der hullschicten des mais kornes. Bot. Arch. 32:392.
HOSENEY, R. C., ZELEZNAK, K., and ABDELRAHMAN, A. 1983. Mechanism of popcorn popping. J. Cereal Sci. 1:43.
HSU, K. H. 1984. A theoretical approach to the tempering of grains. Cereal Chem. 61:466.
KENT, N. L. 1975. Technology of Cereals. Pergamon Press: Oxford, U.K.
PARK, S. W., and KYLE, B. G. 1975. Sorption kinetics and equilibrium of carbon tetrachloride on wheat. Cereal Chem. 52:611.
SCHROETER, L. C. 1966. Sulfur Dioxide Applications in Foods, Beverages, and Pharmaceuticals. Pergamon Press: Oxford, U.K.
SEMENIUK, G. 1954. Microflora. Pages 77-151 in: Storage of Cereal Grains and Their Products. J. A. Anderson and A. W. Alcock, eds. American Association of Cereal Chemists: St. Paul, MN.
VanCAWENBERGE, J. E., ECKHOFF, S. R., BOTHAST, R. J., and ANDERSON, R. A. 1982. A comparison of the trickle-ammonia process with the trickle sulfur-dioxide process for drying high-moisture corn. Trans. ASAE 25:1431.
WOLF, M. J., BUZAN, C. L., MacMASTERS, M. M., and RIST, C. E. 1952. Structure of the mature corn kernel III. Microscopic structure of the endosperm of dent corn. Cereal Chem. 29:349.

[Received February 10, 1988. Revision received August 16, 1988. Accepted August 19, 1988.]