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VOC Emissions from Production of Reinforced Composite Sheet Molding Compound

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ABSTRACT

This paper presents a functional equation for the prediction of VOC emissions from the production of sheet molding compound (SMC) used to form reinforced plastic composite parts. The underlying model was conceptualized based on the results of controlled laboratory studies, and was fit to field data via regression of emission test results against key operating parameters. The field data were collected during Method 204-compliant VOC emission tests of seven SMC machines. Operating parameters investigated include exposed wet area, airflow over exposed wet area segments, linespeed, paste temperature, and styrene content of SMC. The proposed model relates hourly emissions to total exposed area of wet paste, which is constant for each SMC machine.

INTRODUCTION

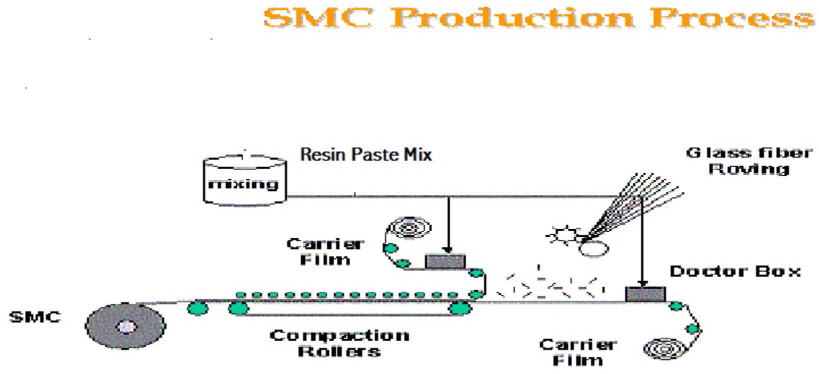
Sheet molding compound (SMC) is used to produce reinforced plastic composite parts in injection and compression presses. SMC consists of resin paste and fiber reinforcement, sandwiched between two nylon-containing carrier films. The volatile component of SMC is the styrene monomer contained in the resin paste, which during molding crosslinks with polymers in the resin paste to form a tough matrix around the reinforcement. On production lines termed “SMC machines,” resin paste is pumped to doctor boxes, from which it is distributed in a thin layer across upper and lower carrier films, which are impervious to styrene. Chopped fibers (typically glass) are spread across the lower carrier film, the two films are brought together, and the final product is either rolled or folded for storage.

Between 2004 and 2008, USEPA Region V required facilities manufacturing SMC in Ohio and Indiana to conduct VOC emission tests to determine compliance with Title V permit conditions. It is believed that a total of eight SMC machines were tested under this program. Results indicated that the emission factors commonly used by these facilities underestimated actual VOC emissions. They also revealed a wide disparity in emissions between machines that were expected to emit similarly. Subsequently, the American Composites Manufacturers Association (ACMA) sponsored the study discussed in this paper, on behalf of compression molders.

The primary objective of this study is to evaluate those test results, and the operating parameters under which they occurred, to derive a functional model (equation) that can be used to predict emissions from SMC machines. The model is needed to provide a credible basis for efficient permitting of this equipment, and to foster pollution prevention through machine and operating modifications. An important secondary objective is to explore the feasibility of using laboratory mass-balance methods to determine what factors drive the generation of emissions. Operating parameters investigated include exposed wet area, airflow over exposed wet area sections, linespeed, paste temperature, and styrene content of SMC.

PROCESS DESCRIPTION

A schematic of the entire SMC production process is given below. Everything shown from the doctor boxes through the compaction rollers is part of the SMC machine. The upstream process, blending or mixing of resin paste, is simplified in this diagram, since mixing commonly occurs in stages.



Adapted from http://www.harveyscomposites.co.za/Information/ApplicationTechniques.aspx

Resin paste from blending is pumped to the upper and lower doctor boxes, reservoirs from which a thin layer of paste is spread over upper and lower carrier films. Carrier films are nylon-containing plastic that have been shown to be virtually impervious to styrene vapor. Glass fiber roving (reinforcement) is pulled through one or more choppers, and the chopped strand is deposited on the paste on the lower film. Downstream, the upper paste-laden film is folded over onto the lower chop-laden film, and the resulting sandwiched SMC is pulled through a series of unheated compaction rollers before exiting the machine, after which it may be rolled, manually folded, or mechanically folded (festooned) for storage.

SMC machines are nominally sized by width. Machines evaluated in this study were 24”, 48”, and 60” wide. For this study, the following dimensions are most critical:

- The width in feet of SMC (wet width W), which may be slightly less than the nominal machine width.
- The total uncovered area in square feet of the doctor boxes (A_d)
- The area of lower bare paste (A_l) = $(Ad/2)+WL_l$ where L_l = the distance measured in feet along the lower film from the point where paste drops onto it to where chop is first deposited.
- The area of upper bare paste (A_u) = $(Ad/2)+WL_u$ where L_u = the distance measured in feet along the upper film from the point where the paste drops onto it to the point where the upper and lower films come together.
- The area of chop covered paste (A_c) = WL_c where L_c = the distance measured in feet along the lower film from the first chop application point to the point where the upper and lower films come together.

SMC emissions consist of styrene monomer (active component of paste resin) that evaporates as paste-laden carrier films traverse the open sections of the line upstream from the compaction rollers. Because film-wrapped SMC traverses the compaction roller section in a matter of seconds, what little styrene would be emitted there would be undetectable during field tests.

ANALYSIS OF EMISSION TEST DATA

Table 1 below describes the seven SMC machines evaluated during this study.

Table 1: SMC Machines Tests Evaluated

Machine	Nominal Width	Facility
1	60"	Meridian Automotive Systems (MAS) Jackson
2	48"	Continental Structural Plastics (CSP) Conneaut
3	24"	CSP Conneaut
4	48"	Molded Fiber Glass (MFG) Ashtabula
5	24"	Zehrco Ashtabula
6	48"	MAS Grabill
7	48"	Premix N Kingsville

Note: CSP Conneaut was owned by Venture Industries when tested

As is typical industry practice, none of these machines employed active measures to control paste temperature at the doctor box. Note that EPA did require testing of an eighth machine, at CSP's Van Wert plant. However, that machine was equipped with active temperature control at the doctor box, which could affect emissions. Because that machine was atypical, its test results were conservatively excluded from the emission model derivation.

None of these machines was tied to a VOC control device. As such, each was located in a large room or open production bays spacious enough to allow forklifts to transfer materials to and fro. Spot ventilation was typically provided in the area of the lower doctor box, primarily to remove glass dust from the roving choppers. Over the open length of most machines, there were either no other spot exhaust pickups or low-flow pickups below the level of the carrier film.

During each of these tests, a Method 204A Temporary Total Enclosure (TTE) was constructed around the SMC machine, including the compaction roller section, to ensure that 100% of emissions generated were captured. The VOC content of inlet (background) and exhaust streams was determined by Flame Ionization Detector (FID). Detector response was calibrated against styrene. All tests were accepted by Region V as valid. ECRM reviewed the test reports, evaluated the design of TTEs and interviewed facility personnel who witnessed the tests, to determine whether any facet of TTE operation caused a test artifact (such as temperature elevated beyond that outside the TTE) that would substantially bias test results - none were identified.

Table 2 summarizes reported test results, dimensional measurements, and operational data provided by plant personnel for each of three test runs (a-c) on each machine. The yellow-shaded columns are parameters that were evaluated via regression analysis against hourly emissions determined during the tests. Those emission test results are given in the blue-shaded column.

Table 2: SMC Machine Parameters and Emissions

	SMC Run lb/hr	Styrene Wt% in SMC	Styrene Run lb/hr	Line Speed ft/min	SMC Width, ft	SMC Area Run, ft2/hr	Upper Bare Paste Length, ft	Upper Bare Paste Area, ft2	Lower Bare Paste Length ft	Lower Bare Paste Area ft2	Length of Paste under Chop, ft	Paste Area under Chop ft2	Open Doctor Box Area, ft2	Total Wet Area	Predicted Emissions	Actual VOC Emitted During Test	Model Residual lb/hr
Test Run	R1	S%	R2	V	W	R3 = 60*W*V	Lu	Au = Lu*W + Ad/2	Ll	Al =Ll*W + Ad/2	Lc	Ac = W*Lc	Ad	At = Al + Au + Ac	Ep =0.1457*At-0.1454	Ea	Ea-Ep
1a	11,713	19.30%	2,261	33.35	4.88	9,755	3.17	19.80	7.79	42.35	8.42	41.03	8.73	103.18	14.89	13.44	-1.45
1b	11,819	19.30%	2,281	33.65	4.88	9,843	3.17	19.80	7.79	42.35	8.42	41.03	8.73	103.18	14.89	15.49	0.60
1c	8,348	19.30%	1,611	23.77	4.88	6,952	3.17	19.80	7.79	42.35	8.42	41.03	8.73	103.18	14.89	15.21	0.32
2a	10,283	10.68%	1,098	34.06	3.92	8,004	0.58	3.18	2.58	11.02	3.17	12.40	1.80	26.60	3.73	3.95	0.22
2b	10,240	10.68%	1,094	33.91	3.92	7,970	0.58	3.18	2.58	11.02	3.17	12.40	1.80	26.60	3.73	4.35	0.62
2c	9,821	10.68%	1,049	32.53	3.92	7,644	0.58	3.18	2.58	11.02	3.17	12.40	1.80	26.60	3.73	4.35	0.62
3a	2,482	14.54%	361	24.35	2.00	2,922	0.83	2.28	1.17	2.94	2.92	5.83	1.22	11.06	1.47	0.869	-0.60
3b	2,566	14.06%	361	25.18	2.00	3,021	0.83	2.28	1.17	2.94	2.92	5.83	1.22	11.06	1.47	0.849	-0.62
3c	2,596	13.90%	361	25.47	2.00	3,057	0.83	2.28	1.17	2.94	2.92	5.83	1.22	11.06	1.47	0.863	-0.60
4a	9,940	11.93%	1,186	44.14	3.83	10,152	2.25	8.63	1.50	5.75	3.42	13.10	0.00	27.47	3.86	4.33	0.47
4b	10,609	11.93%	1,266	47.11	3.83	10,835	2.25	8.63	1.50	5.75	3.42	13.10	0.00	27.47	3.86	3.92	0.07
4c	9,854	11.93%	1,176	43.76	3.83	10,064	2.25	8.63	1.50	5.75	3.42	13.10	0.00	27.47	3.86	3.57	-0.29
5a	4,017	15.47%	621	37.02	2.00	4,443	2.00	4.00	2.00	4.00	1.92	3.83	0.00	11.83	1.58	0.96	-0.62
5b	3,509	15.47%	543	32.34	2.00	3,881	2.00	4.00	2.00	4.00	1.92	3.83	0.00	11.83	1.58	1.45	-0.13
5c	3,866	15.47%	598	35.63	2.00	4,276	2.00	4.00	2.00	4.00	1.92	3.83	0.00	11.83	1.58	1.26	-0.32
6a	9,507	13.80%	1,312	39.82	4.00	9,558	3.50	14.25	3.00	12.25	7.00	28.00	0.50	54.50	7.80	7.89	0.09
6b	9,563	13.80%	1,320	40.06	4.00	9,614	3.50	14.25	3.00	12.25	7.00	28.00	0.50	54.50	7.80	7.81	0.01
6c	9,577	13.80%	1,322	40.12	4.00	9,628	3.50	14.25	3.00	12.25	7.00	28.00	0.50	54.50	7.80	7.63	-0.17
7a	9,682	11.62%	1,125	45.41	3.83	10,444	1.99	7.63	2.33	8.94	2.33	8.94	0.00	25.52	3.57	4.42	0.85
7b	10,189	12.01%	1,224	47.79	3.83	10,992	1.99	7.63	2.33	8.94	2.33	8.94	0.00	25.52	3.57	4.13	0.56
7c	8,912	14.21%	1,267	41.80	3.83	9,614	1.99	7.63	2.33	8.94	2.33	8.94	0.00	25.52	3.57	3.96	0.39

Regression equations here represent emission models. The regression statistic R^2 measures on a scale from zero to one the degree to which variation in emissions correlates with variation in the dependent model parameter. High R^2 values suggest but do not prove causation - it is possible that the model parameter might by chance correlate with emissions or with the true causative factor - so it is important that the model make sense functionally given fundamental physical and chemical principles.

Of the four models, three are simple empirical loss equations: emissions are a function of some measure of throughput. The fourth is a functional model. Based on laboratory studies described below, a predictive function of key variables was derived and then simplified, based upon reasonable assumptions, to a single-parameter predictor. VOC test results were regressed against that predictor. The resulting functional model proved far superior to the throughput models, so it will be considered first.

Experimental Basis of Functional Model

The form of this model was suggested by the outcome of laboratory experiments conducted by one of the authors (Piper) and others at the MFG Research Company, whose parent company operates one of the SMC machines involved the Region V field-test program. A report of that study (1) has been published, but a brief description of the methods and results will suffice here to explain the model derivation. See Appendix A for details of the MFG results.

A test apparatus consisting of a low-velocity wind tunnel with a variable-speed fan was fitted to a digital scale such that a sample pan of resin paste could be quickly introduced with its surface parallel to the floor of the tunnel. The area of the sample pan was 0.16379 ft^2. Cumulative emissions (weight loss) E in grams per second (the average of tenth-second scale readings) were plotted against cumulative exposure time in seconds, to explore the impact of styrene content, air velocity, glass cover, and paste temperature on emissions. Air velocity was measured with a hot-wire anemometer. Typically six to eight replicates are run of each experiment.

A primary goal of the MFG study is to compare emission estimates derived from these weight loss experiments to emissions recorded during the field test of the MFG machine. To establish the experimental conditions, the open area of the machine was first subdivided into upper and lower sectors of bare paste and a sector of chop-covered paste, consistent with descriptions given on page 2. Air velocities at the paste surface across these areas had been recorded with a hot-wire anemometer shortly after the field test, along with mix temperature, machine dimensions, linespeed, styrene content, and glass cover percentage. Mix temperature, styrene content, and glass cover content run during the field test define the “standard paste.”

Weight loss experiments were then run using the standard paste under air velocities matching those in each exposed section of the line. Three observations influenced the form of the functional model.

Styrene Content

Styrene content of SMC had virtually no effect on the weight loss experiments. Styrene content ranged from 13% to 100% (neat styrene). Even the emission curve (cumulative sample weight lost vs cumulative exposure time) for neat styrene substantially overlapped the curves for paste within the relevant exposure time range.

Exposure Time

Best-fit emission curves for upper and lower bare paste sections were mild power functions of exposure time:

$E = k_1T^{c}{}_{1}$ (Equation 1)

where

E = emissions per square foot of paste = sample weight loss/0.16379, g/ft^2
k_1 = proportionality multiplier
T = cumulative exposure time (= time for paste to traverse open length), s
c_1 = exponent

Both k_1 and c_1 were found to be influenced by air velocity over the paste surface and temperature of the paste. As velocity and/or temperature increased, k_1 increased, and c_1 decreased from a maximum value of 1.0 to approximately 0.6.

The emission rate from open bare paste segments on any line can be derived by differentiating Eq1 with respect to T and multiplying by the associated open area. The following equation can be derived to calculate the emission rate in traditional units of pounds per hour.

$E_o = 3600{*}A_oE = (3600/453.6)A_ok_1c_1T^{(c}{}_{1}{}^{-1)} = kA_oT^c$ (Equation 2)

where

E_o = emission rate from open bare paste segment, lb/hr
A_o = area of open bare paste segment, ft^2
k = new proportionality multiplier = $(3600/453.6)k_1c_1$
T = cumulative exposure time, s
c = new exponent = $(c_1\text{-}1)$, which will range from 0 to -0.4

Exposure time is inversely related to linespeed, which in turn is directly related to SMC run, styrene run and SMC area run, the three throughput parameters evaluated in this study by regression against field data. If the emission rate given by Equation 2 were proportional to throughput, we would expect the value of c very close to 1. Since c never exceeded zero in the weight loss studies, the laboratory data suggest that the throughput models will have marginal predictive value. Note that when c is zero, Equation 2 can be simplified as follows.

$E_o = kA_oT^0 = kA_0$ (Equation 3)

Here the emission rate depends only on the area of the emitting wet surface. This condition was observed when tests were run at surface air velocities below 100 feet per minute.

Chopped Glass Cover

For all temperatures and airflows evaluated, the weight loss of paste covered with a loose layer of chopped glass roving was lower than the weight loss from bare paste. This makes sense because the chop cover creates drag over the paste surface, reducing sensible air velocity at the paste-air interface.

On this basis, it is reasonable to assume that c_1 in Equation 1 will be very close to 1, meaning the exponent c of T will be essentially zero. Hence by Equation 3 the emission rate E_c from covered paste will be k_2A_c where k_2 is expected to be somewhat lower than k.

Functional Model Evaluation

A full functional equation could be written by extending Equations 2 and 3 to include calculation of k's and c's as functions of average paste temperature in the doctor box and average air velocity over each section of exposed paste on the line. That is indeed the ultimate objective of the MFG lab studies, and data from MFG suggest that such models will be effective. But except for the MFG machine, we have no data on paste temperature and air velocity during the emission tests, so we cannot generate model predictions for any other machine.

However, we can derive a simple predictor from Equation 3.

$$E \sim k_lA_l + k_uA_u + k_cA_c \sim k(A_l + A_u + A_c) = kAt \qquad \text{(Equation 4)}$$

where

E = total emissions from an SMC machine, lb/hr
A_l = static area of lower bare paste on the machine, ft2
A_u = static area of upper bare paste on the machine, ft2
A_c = static area of chop-covered paste on the line, ft2
A_t = total wet area = $A_l + A_u + A_c$
k_l = lower bare paste area proportionality constant
k_u = upper bare paste area proportionality constant
k_c = chop-covered paste area proportionality constant
k = aggregate areal proportionality constant

Equation 4 is based on two simplifying assumptions: that paste exposure time will have no effect on emissions, and that although the individual k's may vary somewhat, in aggregate these differences will not be significant or will average out so that a single k will suffice to characterize emissions. The resulting model is tested by regressing E in lb/hr from source tests against A_t, where the regression coefficient will be k.

Figure 1 gives the Excel regression plot, with the source test results for each machine designated by separate symbols.

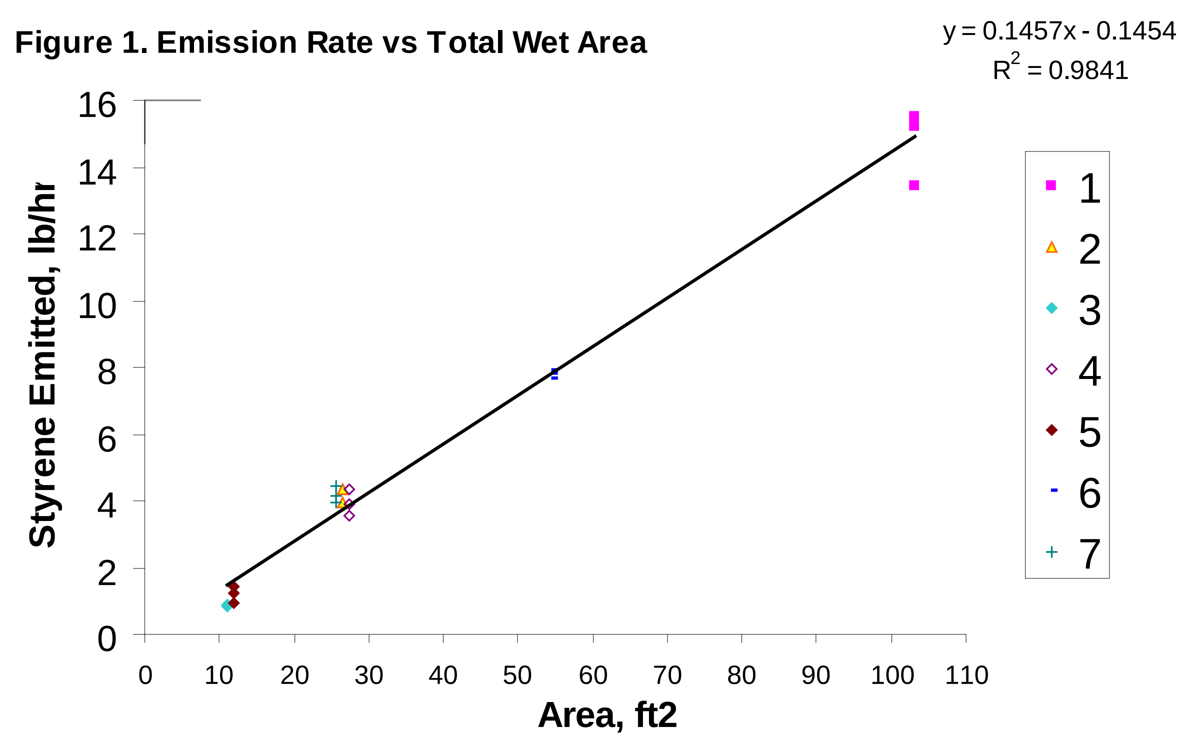


Figure 1. Emission Rate vs Total Wet Area

The very high R^2 value indicates an excellent fit. The resulting emission rate equation is:

$E = 0.1457\ A_t - 0.1454$ (Equation 5)

Equation 5 is broadly consistent with the MFG lab results in that wet area determines emissions. It is instructive to test individual assumptions to determine whether a more complex model might fit the field data even better. A simple way to do this is to plot model residuals (actual emissions - predicted emissions) against parameters of interest, as presented below.

Figures 2 and 3 are plots of model residuals against weight percent styrene in SMC and pounds styrene per square foot of SMC run. Note that styrene content expressed as weight percent is sensitive to the density of filler, which should have no effect on emissions. Styrene content expressed as pounds per area run will be independent of filler density, and hence might be expected to perform better as a predictive variable.

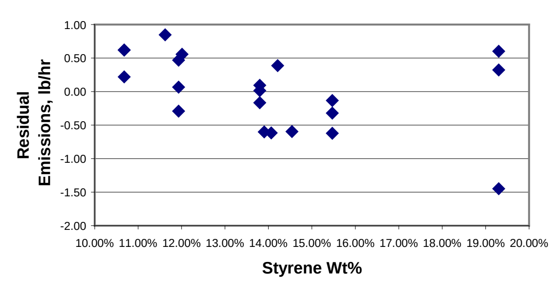


Figure 2. Wet Area Model Residual vs Styrene Wt% in SMC

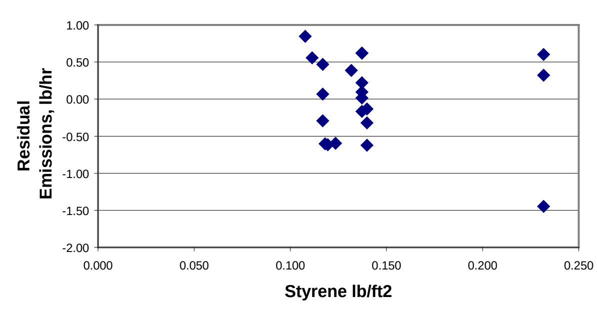


Figure 3. Wet Area Model Residual vs Styrene lb/ft2

Clearly, there is no obvious trend shown in either plot, so the model cannot be improved by incorporating styrene content no matter how it is measured. This is consistent with MFG lab findings that styrene content has virtually no effect on emissions.

Figures 4 and 5 are plots of model residuals against lower bare paste travel (exposure) time and linespeed.

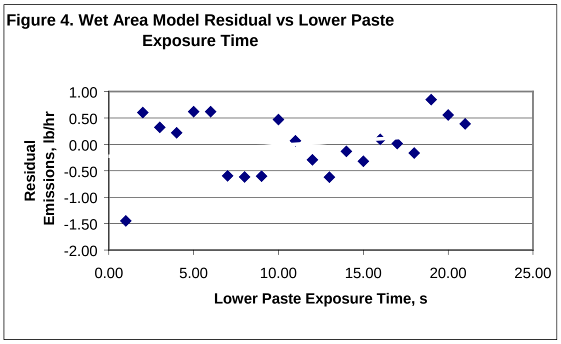


Figure 4. Wet Area Model Residual vs Lower Paste Exposure Time

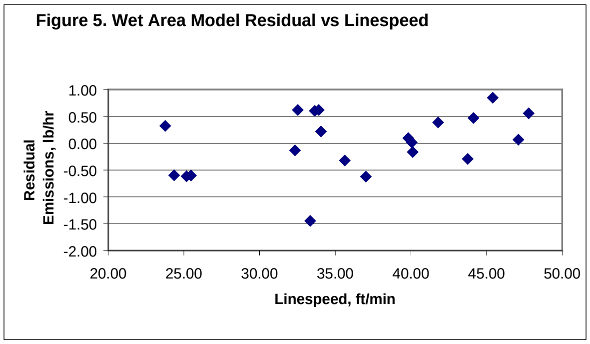


Figure 5. Wet Area Model Residual vs Linespeed

Again, there are no obvious trends, so the model cannot be improved by incorporating either variable. Figure 4 represents the most rigorous test of the assumption that emissions are independent of travel time, since the lower bare paste area is typically closest to exhaust pickups and therefore the likeliest to experience high air velocities. The MFG data suggest that travel time will begin to affect emissions once the air velocity significantly exceeds 100 fpm. In this context, Figure 4 suggests that area-weighted average air velocities are not much higher than 100 fpm over lower paste areas of the tested machines, even though spot velocities could easily be much higher.

Figure 6 is a plot of model residuals against the ratio of total bare paste to covered paste [A_o/A_c, where $A_o = A_u+A_l$].

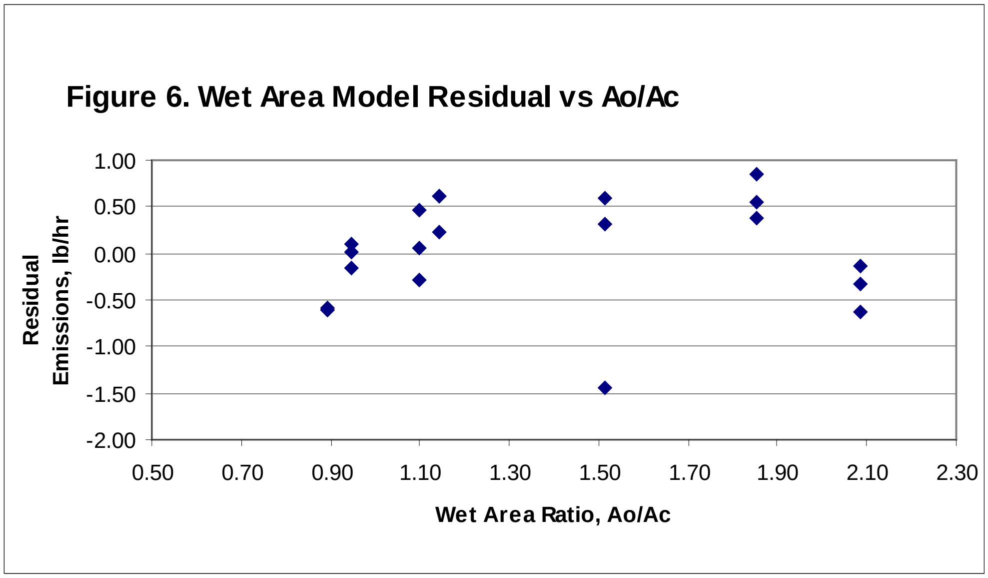


Figure 6. Wet Area Model Residual vs Ao/Ac

MFG study data suggest that Figure 6 might show residuals increasing with increasing areal ratio, since emissions per unit area are expected to be higher from the bare paste sections than from the covered paste section. Yet again, the results show no such trend. This supports our other simplifying assumption that a single proportionality constant k relates emissions to total wet area.

This plot indicates that the model fit cannot be significantly improved by partitioning the wet area into bare and covered sections.

In summary, it is reasonable to conclude that the seven-test fit of the proposed model (relating the emission rate to total wet area) cannot be improved by incorporating any of the additional variables evaluated.

Alternative Models Based on Machine Throughput

Many commonly used emission factors are based on some measure of process throughput rate R. The underlying model is E = f(R), where f(R) may be determined by regressing E against R. The factors currently used in permitting SMC machines are based on the linear model E = f(R) = jR, where R is either SMC or styrene throughput in lb/hr. In other words, predicted emissions are constant fraction j of material run.

For SMC, there are three possible throughput measures, the two mentioned above plus surface area run $A_{r.}$ The latter is suggested by this line of reasoning: since emissions vary with surface area, on any given machine, emissions running SMC of the same width but different thickness at the same linespeed should be the same. Note that A_r in $ft^2/hr = 60*V*W$, where V is the linespeed in ft/min.

Figures 7 and 8 are the regression plots for such models using SMC produced and A_r as throughput variables.

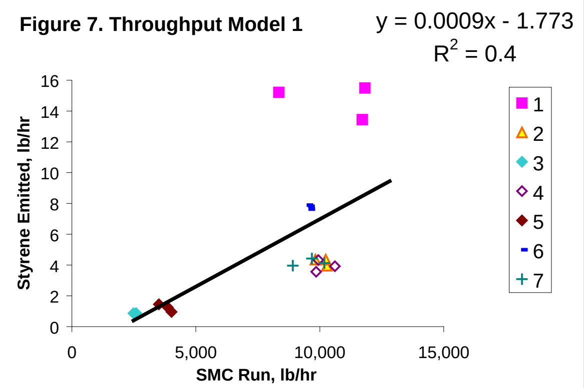


Figure 7. Throughput Model 1

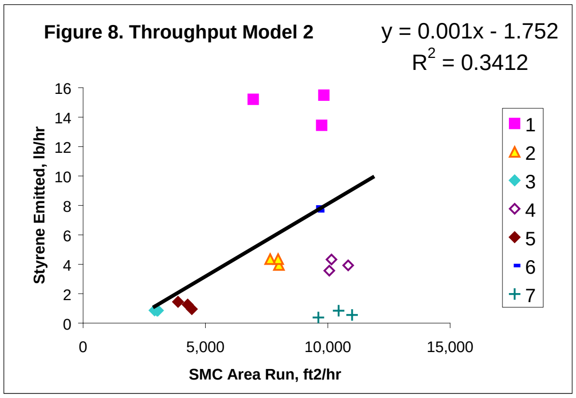


Figure 8. Throughput Model 2

Neither of these variables is useful in predicting emissions, based on the field data. There is extensive scatter around the equation line, and the fit worsens as the machine size increases.

Below are the regression plot of the styrene throughput model (Figure 9) and a correlation plot (Figure 10) that explains the regression results.

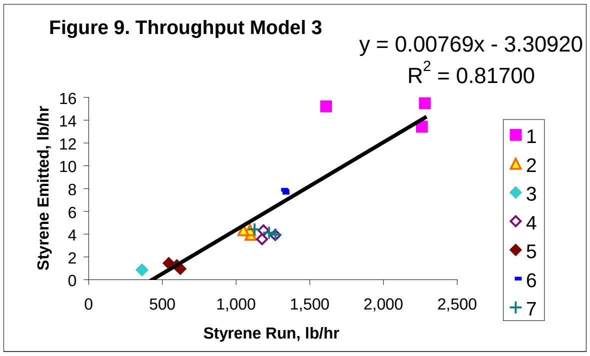


Figure 9. Throughput Model 3

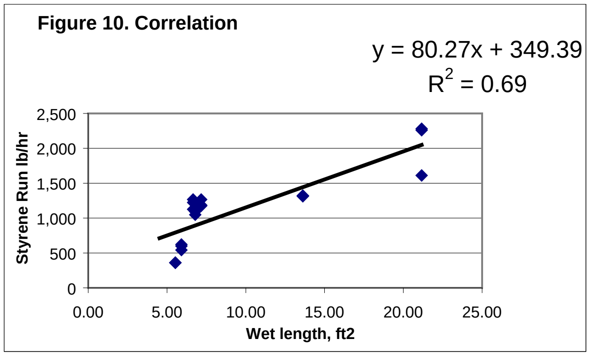


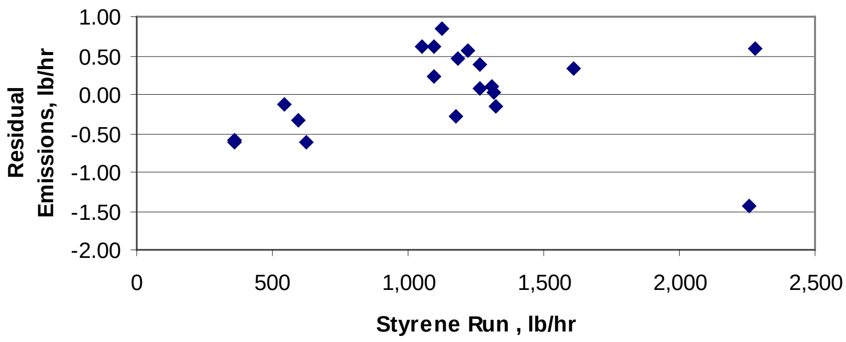
Figure 10. Correlation

The fit of the styrene throughput model is a respectable 82%, though again it worsens for the larger lines. But this model is totally inconsistent with the proposed model and the MFG research, both of which indicate that styrene throughput is irrelevant. The correlation plot suggests an explanation: the fit of the styrene throughput curve is largely the result of a chance correlation between styrene throughput and wet paste length (A_t/W), which we know correlates causally with emissions. There is no obvious causal relationship between wet paste length and throughput - one could modify a machine to change wet paste length without directly affecting linespeed.

The results for 60" SMC Machine 1 further refute the styrene throughput model. That is the only test where the linespeed significantly changed between runs. At the end of the second run (1b), the plant ran out of the resin needed to make paste for the line. A surrogate paste with the same styrene content was mixed by adding excess styrene to another paste recipe using an available resin. However, the line could not run at the same speed with this new material, so the throughput was reduced. For Runs 1a and 1b, the average styrene throughput was 2,271 lb/hr, but dropped 29% to 1,611 lb/hr for Run 1c. However, there was no corresponding drop in measured emissions; they actually increased slightly from 14.47 to 15.21 lb/hr.

Finally, a plot (Figure 11 below) of proposed model residuals against styrene throughput shows very poor correlation, indicating that incorporating this parameter would not improve the model.

Figure 11. Wet Area Model Residual vs Styrene Run



PERMITTING IMPLICATIONS OF THE PROPOSED MODEL

The authors are proposing this model for inclusion in AP-42, the widely-recognized "bible" of industrial process emission calculations. For this purpose, it is not enough that the model successfully predict emissions. With respect to air permits, the model must enable *practical* calculation of both unrestricted potential emissions (to specify applicable emission limits) and actual emissions (to gauge compliance with those limits). Practical calculations involve variables that can be readily measured in the plant environment and easily verified

The proposed model involves a single parameter A_t for each SMC machine, which is easily measured and constant unless the machine configuration changes. Since hourly emissions are invariant, hourly actual and potential emissions are equivalent. Annual potential to emit is simply the resulting hourly emission rate times the maximum allowable hours of operation (8760 hours unless restricted by enforceable permit limits).

It is important to emphasize that the model predicts SMC machine emissions during the time when paste is being applied on the line. The emission test data reflect such operation, since test runs commonly lasted one hour. But even when running optimally, all machines must be shut down periodically during an operating shift to allow carrier film rolls to be replaced. Hence actual emissions will be overestimated if the duration of such periodic shutdowns is not subtracted from run time. For example, a machine running three shifts but down a total of two hours during that time would overestimate daily emissions by about 9% if those emissions were calculated based on a 24-hour day.

Finally, it is prudent to consider the conditions under which SMC machine emissions would not be effectively predicted by the proposed model. The MFG lab studies clearly indicate that paste temperature and air velocity directly affect emissions over open paste areas. Paste temperature variability is somewhat constrained by processability - too low and the paste flows too slowly to run economically, too high and the paste flows off the carrier film. Air velocity over chop-covered paste is also limited because at some point airflow will disturb the glass layer. Air velocity over bare paste is limited by practical considerations. Excessive spot ventilation near choppers will pull glass away from the paste surface, and there is simply no reason to provide aggressive ventilation over quiescent bare paste - worker exposures to styrene vapor are moderated by room dilution over much of the bare paste area.

Note however that for an SMC machine located in a Method 204-compliant permanent total enclosure (PTE) tied to an emission control device, the ventilation regime would be different than if the machine were uncontrolled, even if it were located in a TTE. The presence of an enclosure removes the worker exposure reduction attributable to dilution. In a proper TTE designed to mimic the open shop ventilation regime, this is not a problem because the test runs are short and workers can be instructed to spend as little time as possible in the TTE. In contrast, a PTE would be designed to limit worker exposures no matter how long they remain in the enclosure. Hence the lost exposure reduction due to lack of dilution must be offset by closer capture (more pickups closer to wet surfaces) and/or increased airflow to reduce styrene concentrations in the worker breathing zone.

The net effect is that average air velocities over the wet areas of machines in PTEs would likely be higher than they would if the machines were uncontrolled and in TTEs. Since the model was derived by regression of test results from seven uncontrolled machines located in TTEs, it is reasonable to expect that the model would <u>underpredict</u> emissions vented to a control device from an SMC machine in a PTE.

CONCLUSIONS

The following equation may be used to predict the VOC emission rate E (lb/hr) for an SMC machine.

$\mathbf{E = 0.1457\,A_t - 0.1454}$ (Equation 5),
where
$A_t = A_l + A_u + A_c$
A_l = static area of lower bare paste uncovered by carrier film on the machine, ft^2
A_u = static area of upper bare paste uncovered by carrier film on the machine, ft^2
A_c = static area of chop-covered paste uncovered by carrier film on the machine, ft^2

The regression coefficient R^2 is 0.984, indicating that virtually all of the variation in hourly VOC emissions among the seven tested machines is explained by this model. Model coefficients are consistent with expectations based on preliminary laboratory research at MFG.

No other parameter investigated predicts emissions in the field as well as total wet area. Emissions do not correlate well with linespeed or throughput of SMC, whether measured on a weight or areal basis. Styrene content of paste has no discernible impact on SMC machine emissions. These findings are consistent with those of MFG Research.

The model is conservative, in that it estimates emissions only during times when paste is on the line. For many SMC machines, an emission test with runs exceeding one hour would result in lower reported hourly emissions, because paste would inevitable be off the line for short intervals while carrier film rolls are being replaced, although that time may be included in the reported run time.

The model is expected to underpredict uncontrolled emissions from SMC machines installed in Method 204-compliant permanent total enclosures ducted to control devices.

REFERENCES

1. Piper, Christine, “Mass Balance Determination of Emission Factors for the Production of Sheet Molding Compound” - published by ACMA
2. “Zehrco-Giancola Composites Inc. - Report (of) Emissions Testing - Sampling Performed on SMC Machine Enclosure Outlet” by Custom Stack Analysts LLC, 9/18/06.
3. “Test Results: Fugitive Styrene and VOC Emissions from the SMC Machine at the MFG Plant in Ashtabula, Ohio using the TTE Method” by Engineering Environmental Consulting Services, 10/10/06.
4. “Compliance Stack Emission Test Report - Meridian Automotive Systems (Jackson)” by Air Compliance Testing Inc., 1/9/06.
5. “Compliance Stack Emission Test Report - Meridian Automotive Systems (Grabill)” by Air Compliance Testing Inc., 9/27/06.
6. “Emission Test Report - Determination of Styrene Emission Factors .... 24” SMC Machine (at) Venture Industries, Conneaut, Ohio...” by KBD Technic Inc., 11/15/04.
7. “Emission Test Report - Determination of Styrene Emission Factors .... 48” SMC Machine (at) Venture Industries, Conneaut, Ohio...” by KBD Technic Inc., 12/10/04.
8. “Test Results: Fugitive VOC Emissions from the SMC Machine at the Premix Plant in North Kingsville, Ohio using the TTE Method” by Engineering Environmental Consulting Services, 1/7/08.
9. Biometry, R.R. Sokal and F.J. Rohlf

APPENDIX A: SUMMARY OF MFG WEIGHT LOSS STUDY RESULTS

Fundamental Considerations

Styrene (VOC) emissions from exposed paste on an SMC machine occur due to evaporation, a surficial process. Fundamental mass-transport considerations dictate that evaporative emissions will vary directly and linearly with exposed surface area. After all, the exposed surface is the literally the window through which styrene mass flows from paste below to air above. Further, for any given parcel of paste, styrene can only be emitted during the time in which that parcel travels across the exposed area window, i.e. the exposure time. For each exposed section of length L ft, the exposure time T in seconds is 60*L/V, where V is the throughput parameter linespeed in ft/min.

The MFG lab studies measured cumulative weight loss in grams from samples of SMC paste over cumulative experiment run time in seconds. The surface area of each sample was 0.16379 ft^2, though the initial weight of samples varied slightly with paste density. Hence, graphs of experimental weight loss vs time actually depict the relationship of VOC emissions per unit area of open line to exposure time (travel time across that open area).

Each experiment (e.g. emissions at air velocity *x* and styrene content *y*) in the lab was replicated six to eight times. Using either Excel or the statistical software Minitab, the results were plotted and regression analysis was used to generate a function F(T) that best relates cumulative emissions to exposure time. Equations for the areal emission rate can then be derived though calculus as the derivative of F(T) with respect to T.

Interpretation of Weight Loss Plots in General

All lab experiments generated weight loss regression equations that were power functions of T. The shape of these regression curves is critical to understanding the impact of changes in T on emissions. So before considering specific MFG results, it is instructive to consider in general what these curves look like, and how they should be interpreted.

The generalized power function for areal emissions is:

$E_a = k_1T^{c}{}_{1}$

where: E_a = emissions lb/ft^2

T = exposure time, s

k_1, c_1 = constants

We differentiate this equation with respect to T to get the areal emission rate E:

$dE_a/dT = E = kT^c$, where $k = c_1k_1$ and $c = c_1-1$.

Figures A.1 and A.2 depict respectively four hypothetical weight loss curves and the associated areal emission rate curves.

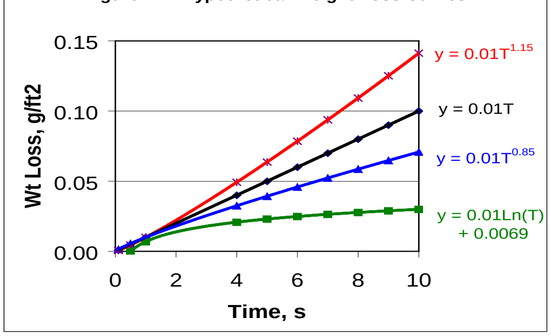


Figure A.1 Hypothetical Weight Loss Curves

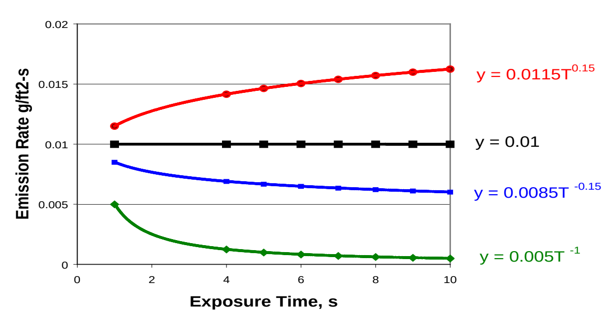


Figure A.2 Emission Rate Curves

In Figure A.1 the value of k in each case has been arbitrarily set at 0.01. Consider first the black curve in each figure. The resulting equation represents the power function at c = 1, which reduces to a linear function. The derivative of this equation as shown in Figure A.2 is a constant, meaning the emission rate is invariant with respect to T. Recall that *for any given machine*, T is an inverse function of the throughput parameter linespeed. Hence, linear weight loss curves (straight lines) imply that the emission rate for a given SMC machine will not vary as linespeed changes. As you will see, several MFG lab experiments yielded results plotting as straight lines.

The blue curve in Figure A.1 represents the power function at c = 0.85. It curves downward from the linear function line. The derivative of this equation as shown in Figure A.2 is another power function, where c = -0.15. The emission rate here decreases nonlinearly as T increases. Since on any machine T varies inversely with linespeed, weight loss curves plotting as power functions with exponents between zero and one imply that SMC machine emission rates will increase nonlinearly as linespeed increases, and vice-versa. Further, the closer that exponent is to one, the lower the impact of linespeed changes on emissions. Several MFG experiments yielded such curves

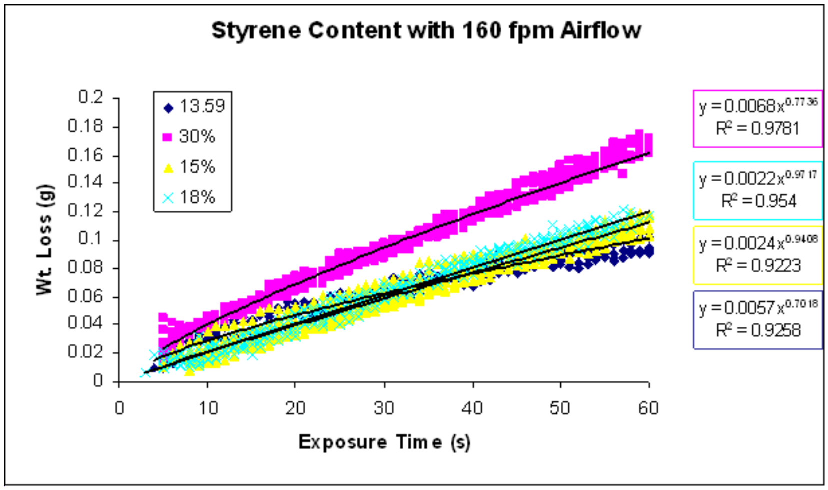
The red curve, which represents the power function at c = 1.15, bends upward from the linear function line. Since the derivative of this equation as shown in Figure A.2 is a power function with c = 0.15, the emission rate here increases as T increases. For the same reasons given above, weight loss curves plotting as power functions with exponents greater than zero imply that SMC machine emission rates will decrease nonlinearly as linespeed increases, and vice-versa. Note that such weight loss curves were never seen in any of the experiments conducted by MFG.

Past agency practice has been to normalize emission factors against throughput. Since all throughput measures vary directly with linespeed, the implied equation for emission rate is E = kV, where V is the linespeed. Further, since V is proportional to $1/T = T^{-1}$, we would expect to see emission rate curves of the form $E = kT^{-1}$. Integrating this equation, we get the associated weight loss equation, $E_a = k\ln(T) + k_1$, where ln(T) is the natural logarithm of T and k_1 is another constant. These two curves are shown in green in Figures A.1 and A.2. The green weight loss curve in Figure A.1 is what we should see in the lab if machine emission rates (lb/ft^2-hr) vary directly with throughput (ft/hr). Logarithmic curves of this type did not fit the MFG weight loss data very well.

Within the context of this general guidance on interpretation of weight loss curves, the following three sections discuss the specific findings of the MFG experiments.

Effect of Paste Styrene Content on Weight Loss

Figures A.3a-b below depict the results of bare paste weight loss experiments where the styrene weight content was varied from 13.59% to 30% under conditions of still air and 160 fpm.



At zero airflow, it is evident that the lines overlap, and statistically there is no difference between the weight loss plots. At 160 fpm, the line for 30% diverges from the others. At exposure times typical of bare paste areas (3-6 seconds), increasing the styrene content by 220% correlated with a weight loss increase of only 29-36%. Note that 30% paste is barely usable and probably represents an extreme worst case. Furthermore, average airflows over bare paste would be expected to be lower than 160 fpm. On balance, it is reasonable to expect that styrene content will have little effect on SMC machine emissions in the field.

Effect of Air Velocity on Weight Loss

Figure A.4 depicts the results of weight loss experiments using the “standard paste” (13.59% styrene at 90F in doctor boxes).

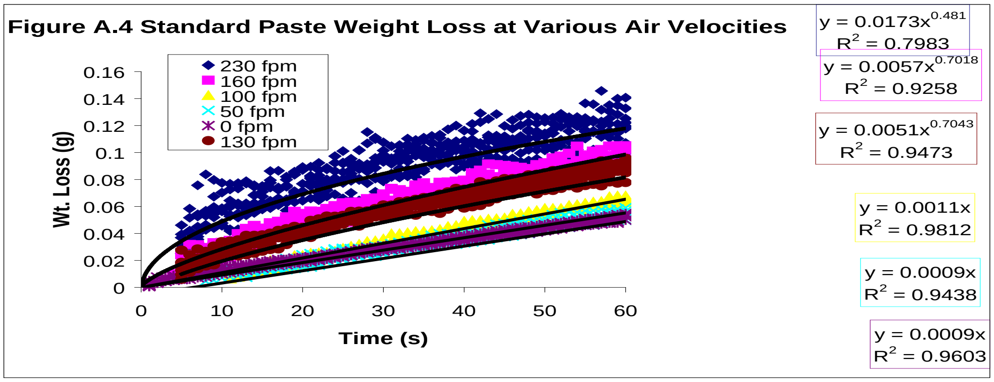
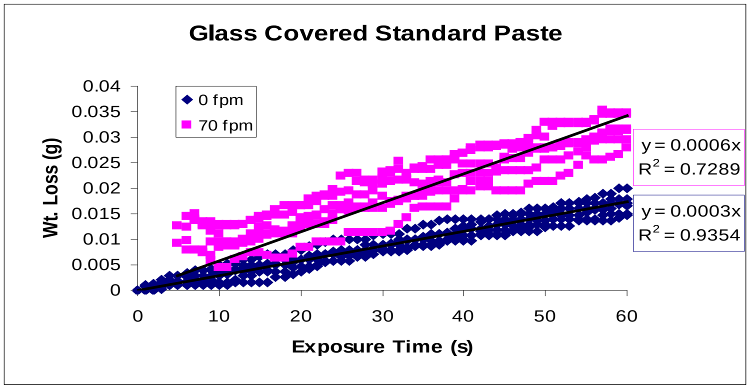


Figure A.4 Standard Paste Weight Loss at Various Air Velocities

Air velocities in the test tunnel were measured by hot-wire anemometer, which is not sensitive to air velocities much below 50 ft/min. At measured air velocities below 100 ft/min, the graphs are linear (exponent $c_1 = 1$). As air velocity increases above 100 fpm, the constant k_1 increases and c_1 decreases. These results imply that beyond 100 fpm only, increasing air velocities over the open paste surface of an SMC machine will increase the areal emission rate and the direct impact of linespeed on the areal emission rate will also increase. The results also imply that below 100 fpm air velocity, linespeed has no effect on the areal emission rate

Effect of Chopped Glass Cover on Weight Loss

Figure A.5 depicts the weight loss of standard paste samples covered with a loose layer of chopped glass. The weight of glass added was consistent with the glass content of SMC run during the field tests at MFG, and the air velocity was set at 0 and 70 ft/min, the latter value being that measured shortly after the test on the machine.


Glass Covered Standard Paste

The weight loss graphs are linear, and k_1 is only 33-60% of what it would have been if the paste were uncovered. Note that scatter between runs increased markedly at 70 fpm. Further, confidence and prediction intervals (not shown) for the regressions overlap in the region of relevant exposure times. These results imply that the areal emission rate from chop-covered paste is likely to be somewhat lower than that from bare paste, and varies little or none with linespeed.