

# **Residual Vinyl Chloride Levels in US PVC Resins -Update**

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# Outline

- Last Presented at ANTEC 2004 and published in JVAT 2005
- Beren's model refresher
  - Desorption Curves Experimental verses Actual
- Stripping Columns
  - Fixed, Operation variables
- Update on residual vinyl chloride monomer (RVCM) in resins from 2000 to 2017
- NSF RVCM in Pipe Chronology data
- Review of FDA food contact information

# Background of VC Regulation

- 1973 - Confirmed diagnosed case of angiosarcoma in worker at B.F. Goodrich facility in Louisville
- 1974 - OSHA issued regulation to reduce workplace exposure from est. 200 to 1 ppm 8 hour time weighted average, with 0.5 ppm action level.
- 1976 - the U.S. Environmental Protection Agency (EPA) further regulated vinyl production process with VC NESHAP
- 1977 - National Sanitation Foundation (NSF) had set a 10 ppm RVCM level for pipe grade resin
- 1986 - NSF sets 2 ppm RVCM level in pipe resin
- 1998 - NSF sets 3.2 ppm RVCM level in pipe in resin
- 2012 – EPA PVC MACT updates VC NESHAP to part 63 rule and institutes most comprehensive regulation on any industry in a single rule i.e. air, water, and product limits.

# US Vinyl Chloride Emissions

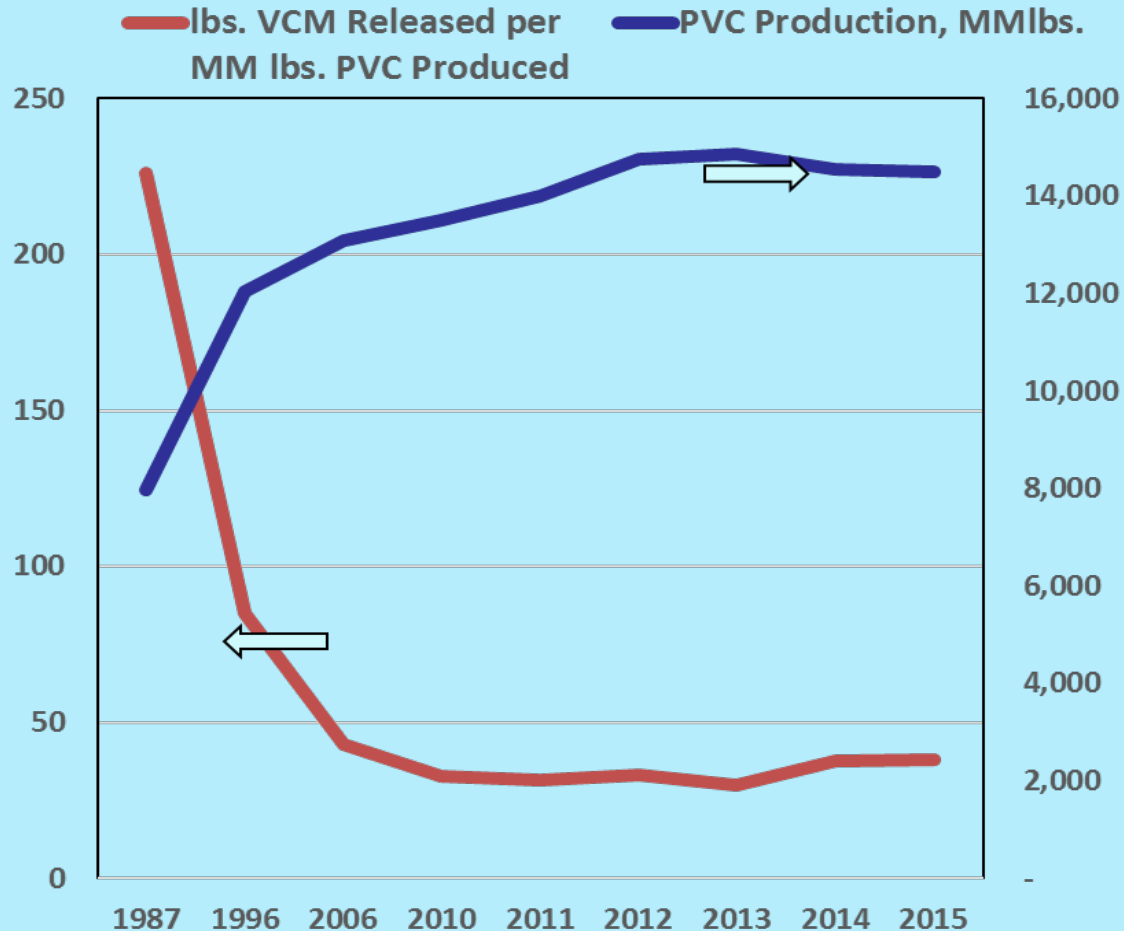
(On Unit Basis, Down 83% Per Lb. Produced Since 1987)

Unit VCM Emissions Have Declined 83% Since 1987

VCM Emissions: Pounds per Million Pounds Vinyl

Vinyl Resin Production Increased by 82% since 1987

Vinyl Production, Million Pounds



# Berens Model of Diffusion ~ 1974

- Berens vapor sorption experiments on PVC powder samples obey simple Fickian kinetics at low VCM concentrations and provide a convenient method of determining the diffusivity of VCM in PVC. This simple model of diffusion in uniform spherical particles predicted that essentially complete monomer removal from particles of diameter under 5 microns could be achieved in a few minutes at temperatures near 100°C.
  - Testing used uniform, spherical, submicron emulsion polymerization PVC particles - a simple, well-defined geometry, favorable for analysis of sorption kinetics, with diffusion dimensions much smaller than in the thinnest feasible polymer films.
  - Using this data one could predict migration of VCM from rigid PVC pipe.

# Desorption of VCM

- Fick's First Law

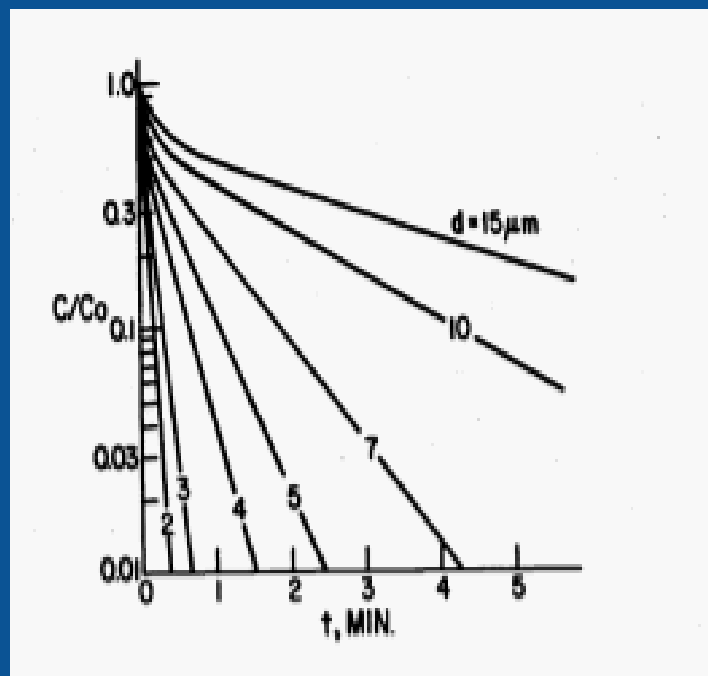
- $F = -D \, dc/dx$

- Which says diffusion across a unit plane area in unit time,  $F$ , is proportional to the concentration gradient ( $dc$ ) across the depth of the plane ( $dx$ ). The proportionality constant,  $D$ , is called the diffusion coefficient.
    - Diffusion constant for pure PVC is essentially the same as compound.
    - Now we need Crank's text that converts this into equations for various shapes.

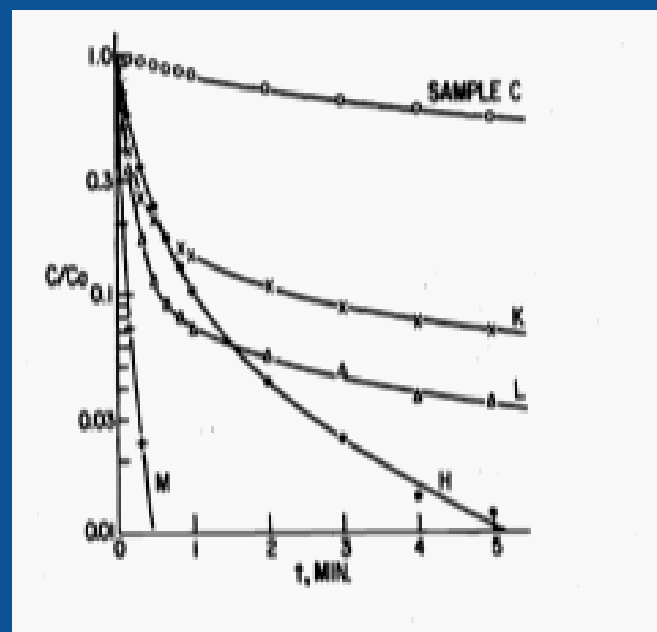
- Using these equations, assumptions and experimental data described in the paper it is concluded that:

- Rigid PVC pipe with 3.2 mg/kg or less will meet 0.0002 mg/kg in drinking water, which is one-tenth the EPA standard.

# Figure 1: VCM Desorption at 90 C Calculated versus Experimental



Calculated VCM desorption vs  
diameter of PVC at 90 C

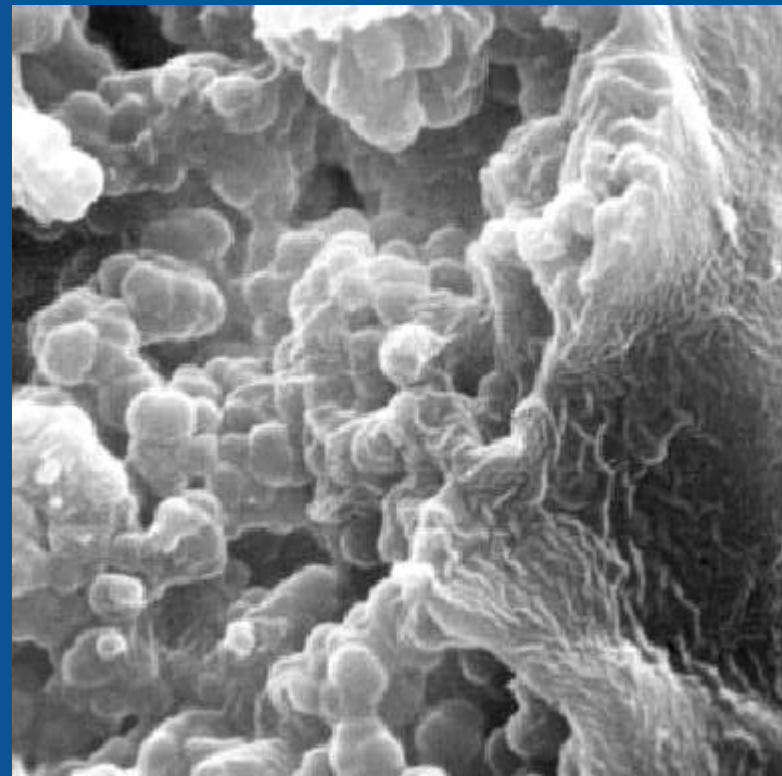


Experimental VCM desorption  
curves S\_PVC at 90 C


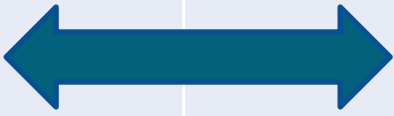
Source: Berens

# Figure 2: Real Particle Size Effects

- **Commercial suspension PVC**
  - Is not 2 microns in diameter like dispersion.
  - It has an average of 150 microns.
  - It has porous areas.
  - It some dense areas.
  - The particle morphology varies depending on molecular weight.
    - Low MW is denser and has higher bulk density.
    - High MW is more porous and has lower bulk density.
- Desorption rates are different depending on resin MW and type. In 2009 there were 120 different suspension products produced



# Figure 3: PVC Factors Affecting Stripping

1-10 microns	10-40 microns	40-100 microns	100-larger microns
Less Porous			More porous
Low Molecular Weight			High Molecular Weight
Emulsion and Dispersion Resins	Micro Suspension Blending Resin	Suspension Blending Resins	Suspension Resins
<b>Harder</b>	<b>Less Hard</b>	<b>Less Easier</b>	<b>Easier</b>

Virgin Mat'l

Recycle

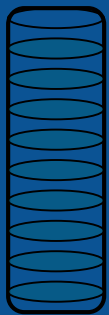
Emission

# Figure 4: PVC Suspension Process and Stripping

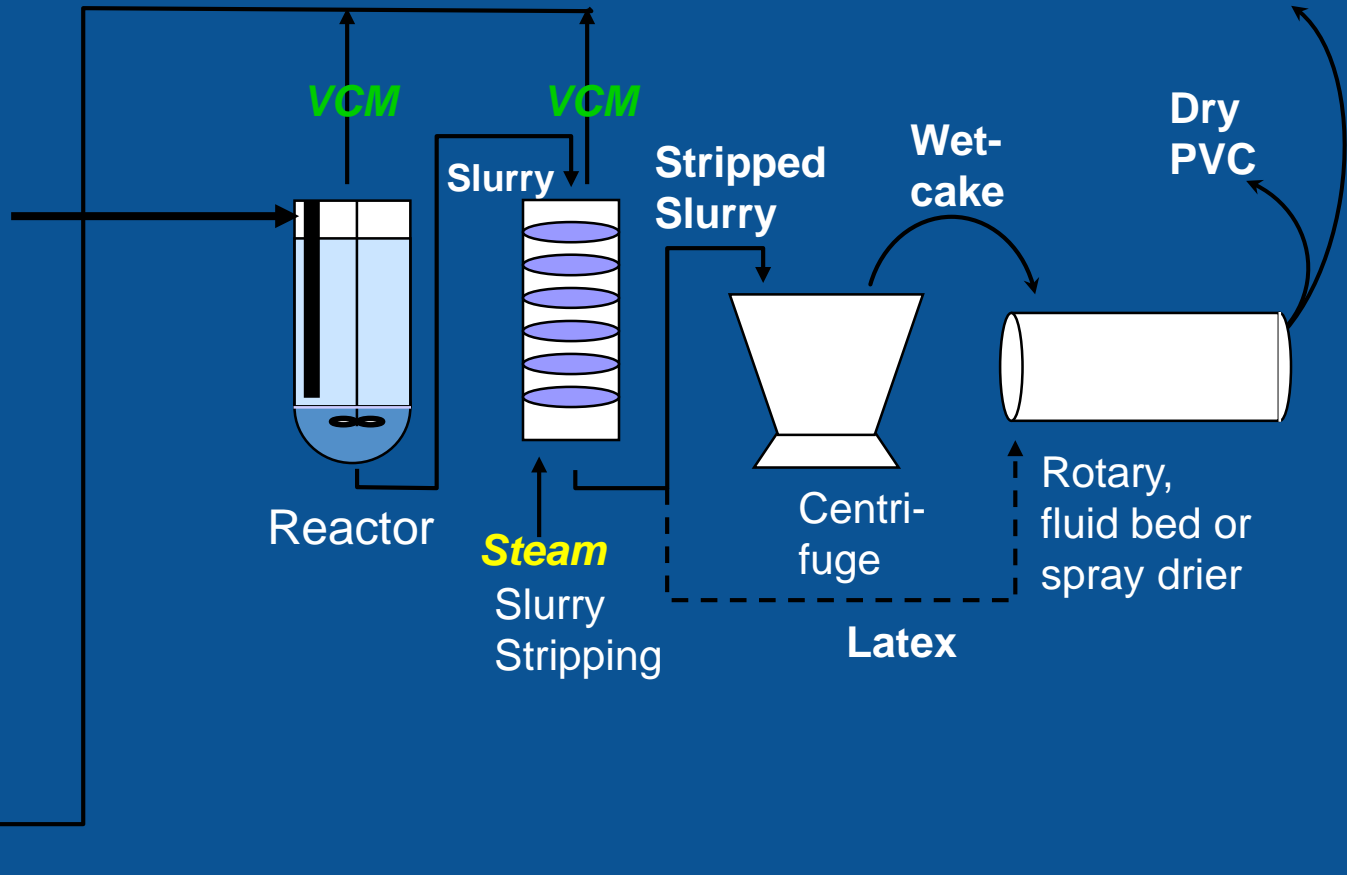
Raw Materials:

VCM, ReVCM, Water, Surfactants, Initiator,

ReVCM



VCM Recovery



H<sub>2</sub>O,  
VCM

Dry  
PVC

Reactor

Slurry

Steam  
Slurry  
Stripping

Stripped  
Slurry

Centri-  
fuge

Wet-  
cake

Latex

Rotary,  
fluid bed or  
spray drier

# Stripping Column Operational Parameters

- **Fixed Column Dimensions**
  - Diameter of column
  - Number of plates
  - Height of the weir
  - Size of the holes in the plates
- **With Fixed Column Dimensions the Variables are:**
  - Column Temperature/Pressure
  - Product Flow Rate
  - Steam Pressure

# Residual Vinyl Chloride Levels

- VI survey of PVC producers in 2000
- VI survey of PVC producers in 2017
- NSF International PVC Pipe and Fittings Testing (1/1/98 through 10/18/2000)

# Table 1: Analytical Test Methods to Measure RVCM

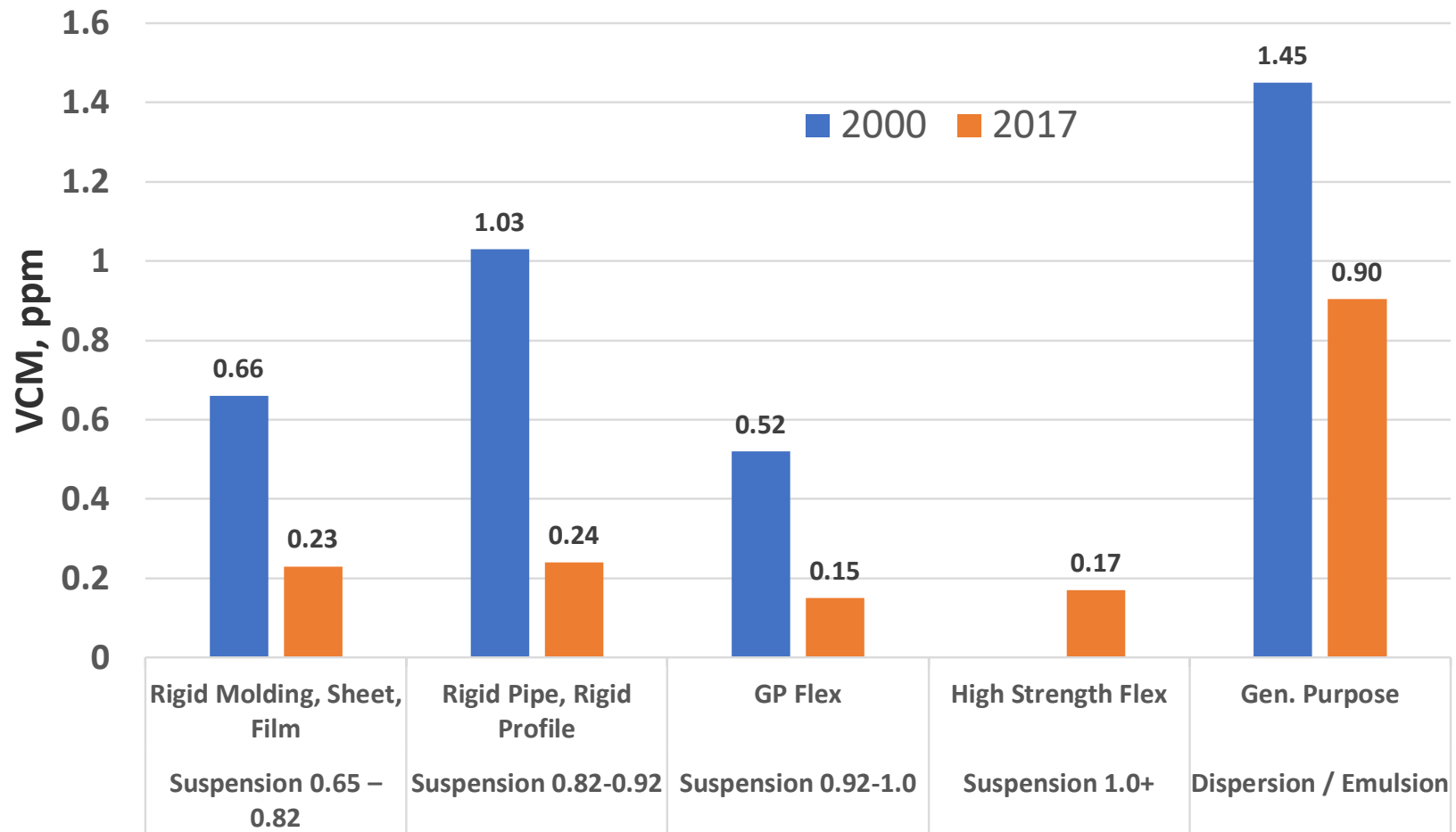
Method	Application	Solvent	Sample Temp, C	Condition time, min.	Analytic Equipment
EPA Method 107	PVC Resins	None	90	60	GC, FID
ISO 6401, or ASTM D4443, or NSF	PVC materials, molded/ extruded/ compounds	N,N'-dimethylacetamide	70	60	GC, FID

## Table 2: Vinyl Institute RVCM Survey Results <sup>[1]</sup> Comparison

<u>Resin Type, IV</u>	<u>Use</u>	<u>Weighted- average RVCM, YTD 2000 (ppm, weight)</u>	<u>Average Typical RVCM 2017, ppm</u>
Suspension 0.65 – 0.82	Rigid Molding, Sheet, Film	0.66	0.23
Suspension 0.82-0.92	Rigid Pipe, Rigid Profile	1.03	0.24
Suspension 0.92-1.0	GP Flex	0.52	0.15
Suspension 1.0+	High Strength Flex		0.17
Dispersion / Emulsion	Gen. Purpose	1.45	0.90

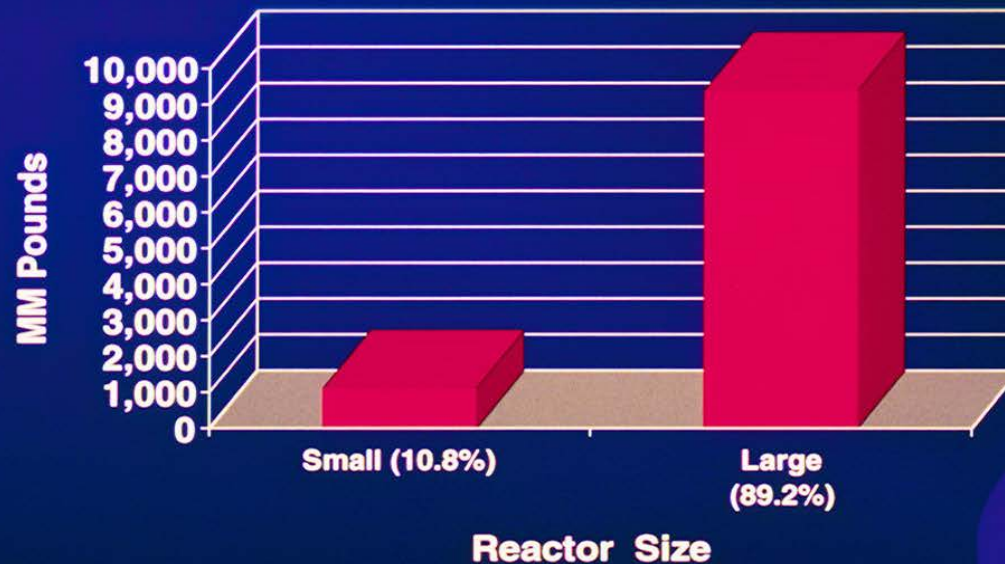
1] Results reflect all VI member company PVC manufacturers, which in 2017 included all US producers

# Figure 5: VCM vs. Resin Molecular Weight vs. Year



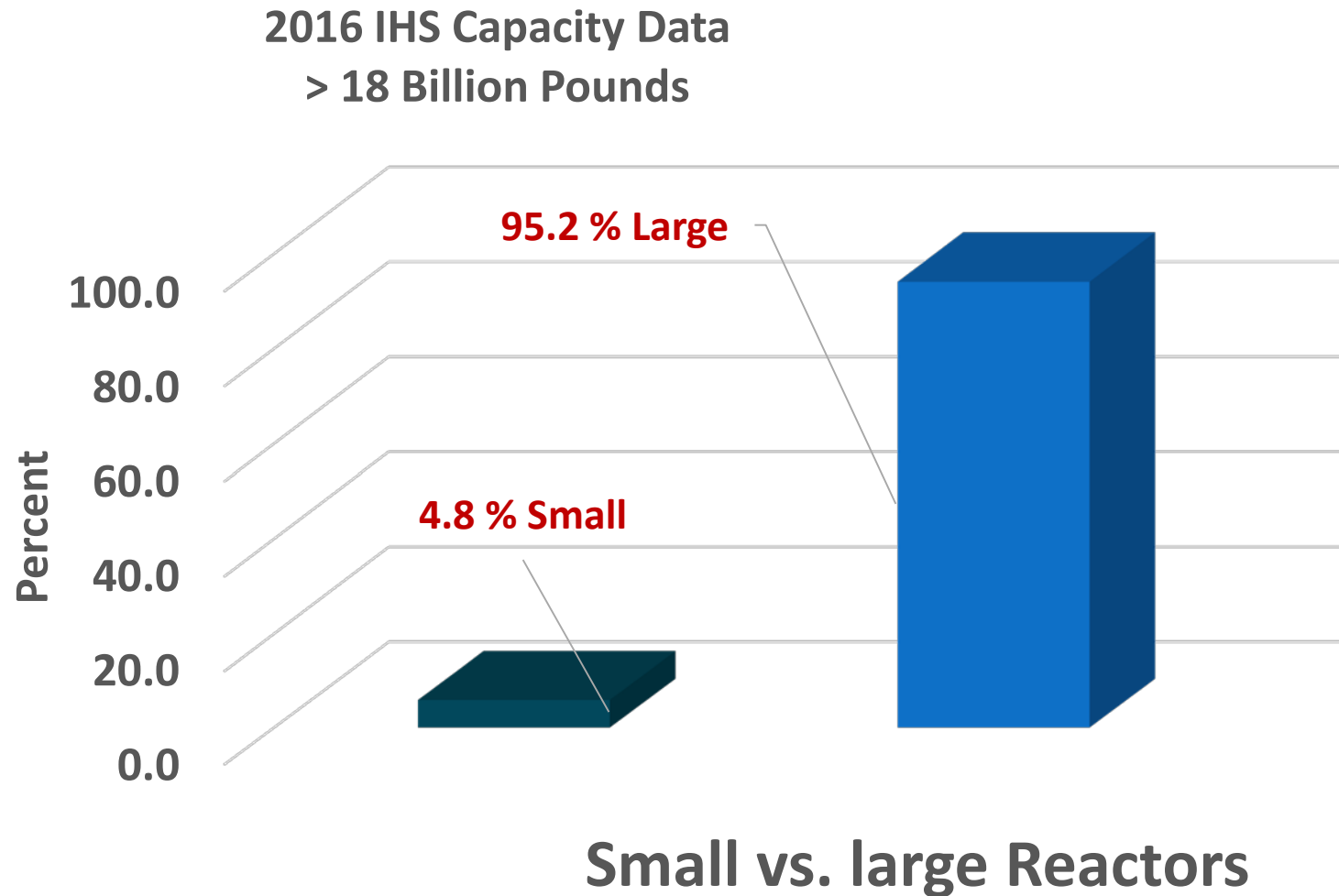
# Figure 6: 1994

## PVC Capacity vs Reactor Size

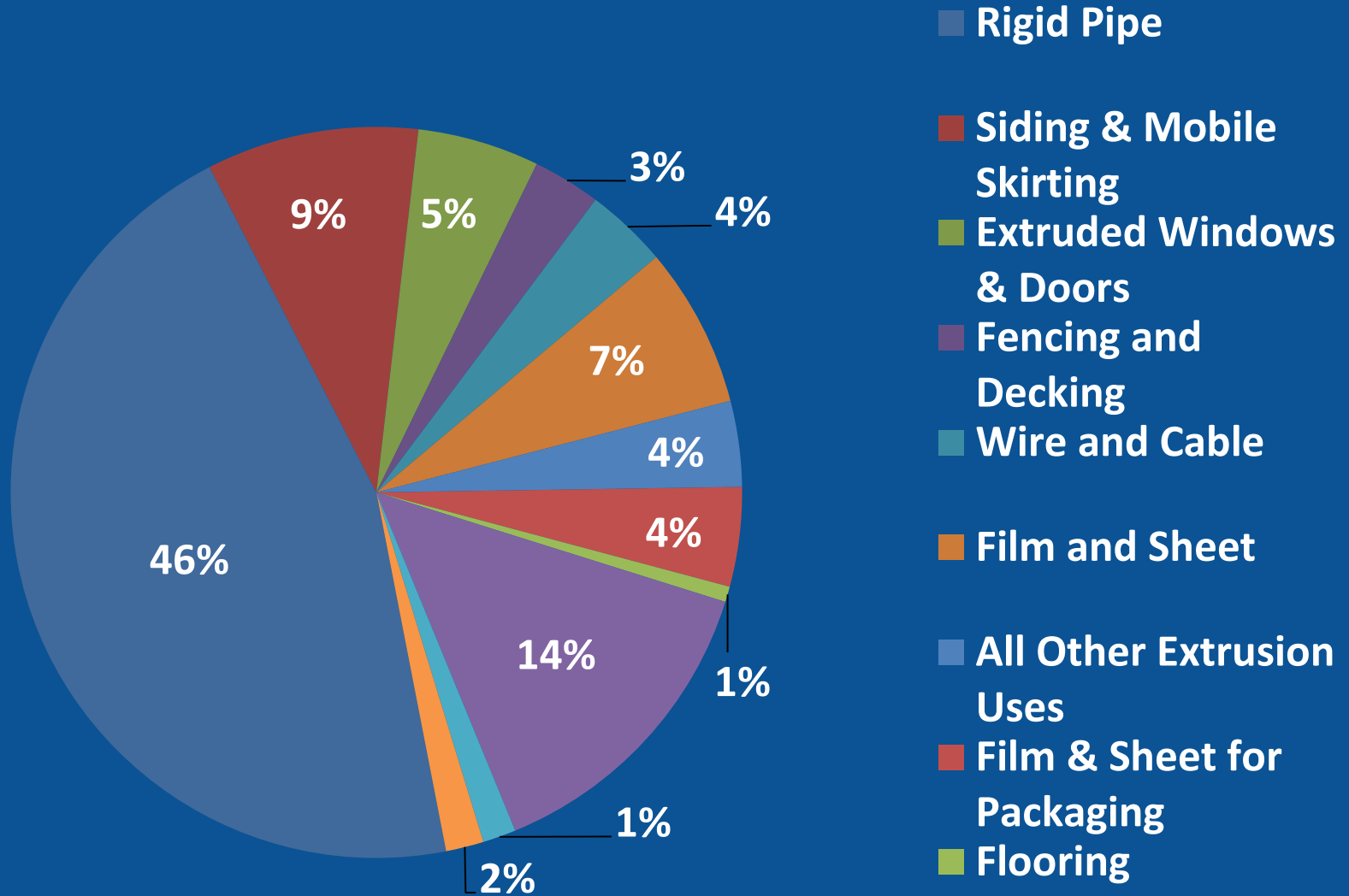


# Figure 7: 2016

## US Capacity by Reactor Size,



# Figure 8: 2016 US and Canada Markets



# Table 3: Why PVC is Good for Pipe

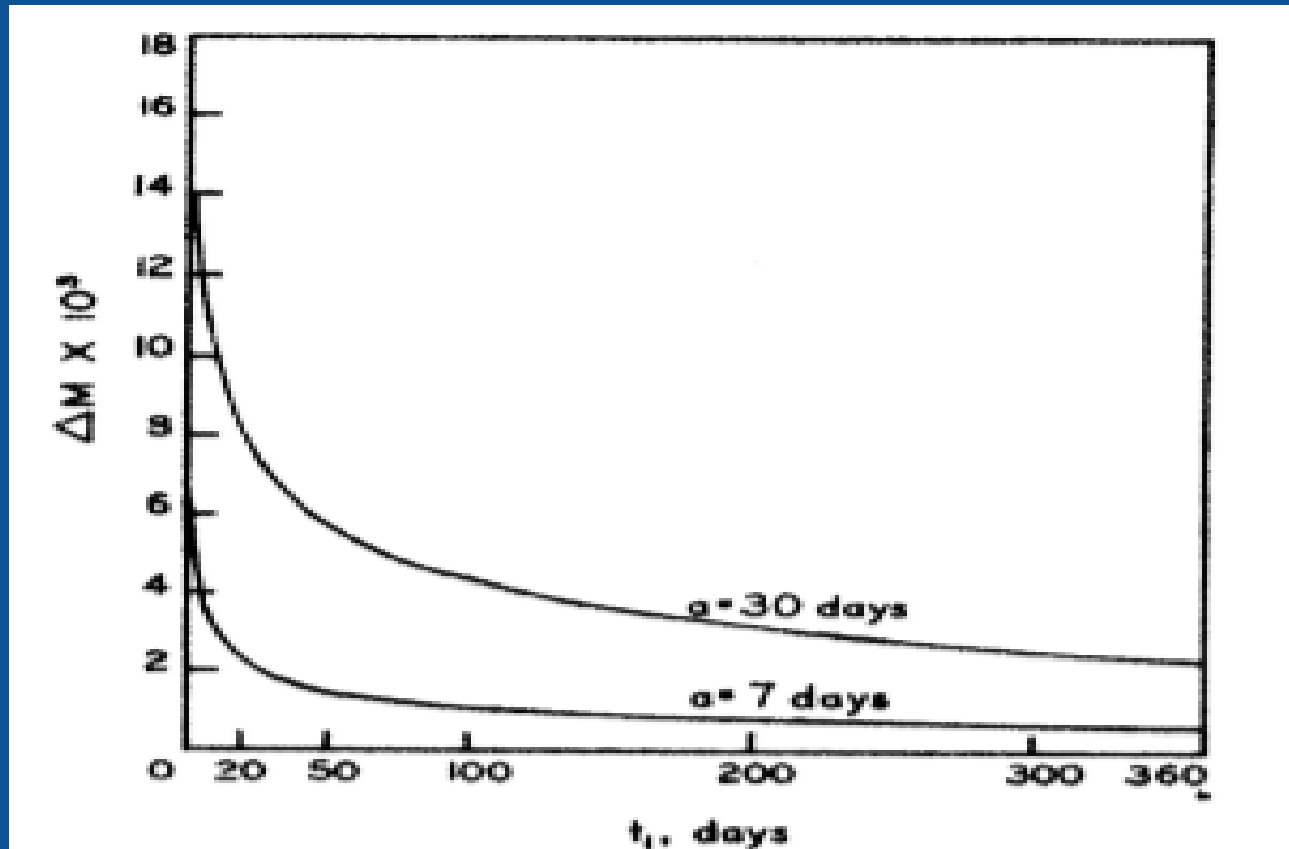
Material	Tensile strength, psi	Flex Mod of elasticity, psi	Izod impact, Ft.-lb./In.	Heat Deflection Temp @ 66/264 psi, deg. F	Water Absorption 24 hrs, wt. %
<b><u>LDPE</u></b>	1,400	30,000	no break	122 -	0.10
<b><u>PP (Copolymer)</u></b>	3,800	215,000	12.5	190 -	slight
<b><u>HDPE</u></b>	4,000	200,000	-	172 -	0.10
<b><u>PP (Homo-polymer)</u></b>	5,400	225,000	1.2	210 -	slight
<b><u>PVC (Rigid)</u></b>	7,500	481,000	1.0	- 158	0.06

# ANSI/NSF Standard 61

- Measures RVCM in product wall using GC
- Diffusion calculation done on 30 day old 1 inch inner pipe diameter with a diffusion time of 16 hours
- Pass/fail value of 3.2 mg/kg is based on a expected concentration in contacted water at 1/10 of the US EPA MCL for vinyl chloride of 2 ug/L or 0.2 ug/l

# Figure 9: Fraction of VCM Entering Pipe Contents

Berens: Prediction of VCM monomer migration from PVC pipe  
1/8 inch wall thickness 30°C



7 and 30 day extraction time verses pipe age at start.  
Pipe sits an average of 2 days before full use.

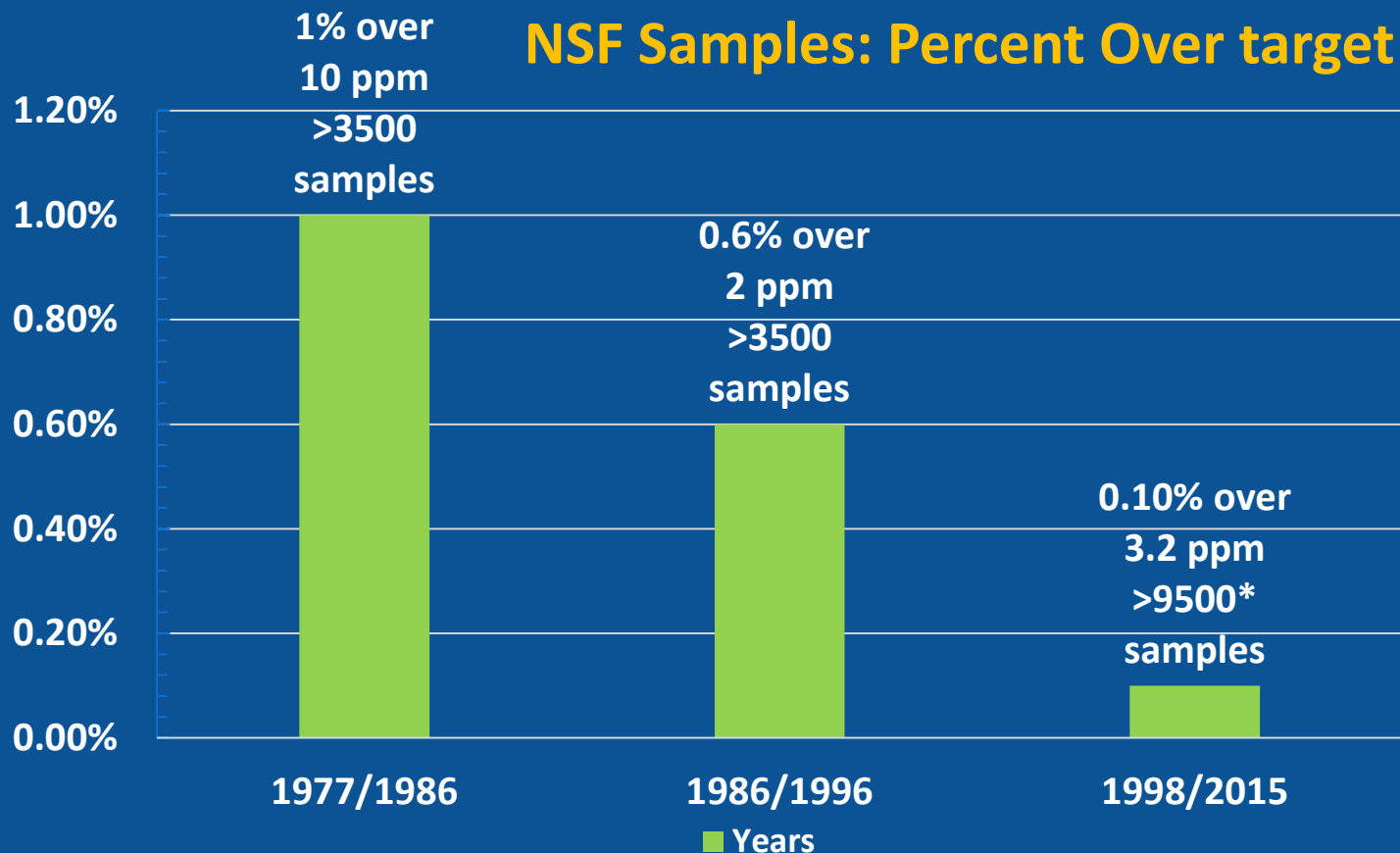
# 2000 to 2015

## NSF Tested Pipe Samples

- 7625 Pipe Samples Tested
- 7363 Samples were non detectable at 0.5 ppm
- Of the 262 samples above ND, 193 were less than 1.0 PPM
- Using zero for ND the average value was 0.036 ppm which is about 50% of the 1998-2000 data.

# Figure 10

## Reduction of RVCM verses Test Period (with Changing Targets)



\* Many > 3.2 ppm were produced off shore

## Table 4: Results of NSF International PVC Pipe and Fittings Testing January 1998- October 2000

	Samples tested	Samples reported as Non-Detect	Percent Non-Detect	Average RVCM in product mg/kg
Pipe	519	445	86	.07
Fittings	178	157	88	.03

NSF has a method sensitivity of 0.5 mg/kg and a level of detection of 0.1 mg/kg

# Table 5: Summary of 2004 Data RESIDUAL VC MONOMER IN FOOD AND NON-FOOD PACKAGING (No FDA Restrictions (51FR4183, Feb. 3, 1986))

## FOUND ON STORE SHELVES

Package description	VCM (parts-per-billion)
1 gal. water jug A	4.7
1 gal. water jug B	5
Mouthwash bottle	3.3
Non dairy creamer jar	< 2
PVC meat wrap A	< 2
PVC meat wrap B	< 2
Saran™ wrap	< 2
Canola oil jug A	1.7
Vegetable oil jug B	2.9
Olive oil jug A	2.4
Olive oil bottle B (n=3)	28.3
Nonfood packaging	
PVC Plumbing blister	135.4
PVC Cell phone blister	3.9

# Overall Conclusions

- **More than 96.6% (2000 was 86 percent) of pipe tested by NSF International were non-detectable for RVCM at 0.1 ppm.**
- **The overall average of RVCM in PVC resin continues to decline compared to 2000.**
- **Reduction of monomer to these levels assures a safe workplace for producing products with vinyl resins and safe products**
- **The U.S. PVC industry continues to grow. With more than 15 billion pounds being produced annually**

# Acknowledgements

- **The Vinyl Institute wishes to acknowledge the participation of its members in providing data, reviewing results, and approving this presentation for publication.**
- **The Vinyl Institute also wishes to acknowledge the substantial contributions to this presentation by NSF International, and Keller and Heckman, legal counsel to VI.**

**Questions?**

**Thank you for your attention**