THE AUBURN ENGINEERING TECHNICAL ASSISTANCE PROGRAM INVESTIGATION OF POLYVINYL ALCOHOL FILM DEVELOPMENTS PERTAINING TO RADIOACTIVE PARTICLE DECONTAMINATION AND INDUSTRIAL WASTE MINIMIZATION.

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Tracey Lawrence Mole

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DISSERTATION ABSTRACT

THE AUBURN ENGINEERING TECHNICAL ASSISTANCE PROGRAM INVESTIGATION OF POLYVINYL ALCOHOL FILM DEVELOPMENTS PERTAINING TO RADIOACTIVE PARTICLE DECONTAMINATION AND INDUSTRIAL WASTE MINIMIZATION.

Tracey Lawrence Mole

Doctor of Philosophy, December, 2005
(B.Ch. E., University of South Florida, 2002)

Directed by Arthur Ray Tarrer.

Formula optimization of new products and improvement of existing merchandise is practiced in many different industries including paints and dyes, polymers and plastics, foods, personal care, detergents, pharmaceuticals and specialty chemical development. Current trends in the engineering design community have moved towards the development of quantitative integrated solution strategies for simultaneous consideration of multiple product characteristics. The optimization variables are most often determined by qualitative attributes, stochastic variables, visual observations and/or design

experience. The effectiveness of these approaches is limited by available data, bias towards specific solutions and experimental error and reproducibility. Model insight is required for development of fast, reliable and systematic screening methods capable of identifying optimal formulations and reducing the number of subsequent laboratory experimentations.

In this work, an effective and systematic model is devised to synthesize the optimal formulation for an explicit engineering application in the nuclear industry, i.e. radioactive decontamination and waste reduction. Identification of an optimal formulation that is suitable for the desired system requires integration of all the interlacing behaviors of the product constituents. This work is unique not only in product design, but also in these design techniques. The common practice of new product development is to design the optimized product for a particular industrial niche and then subsequent research for the production process is conducted, developed and optimized separately from the product formulation. In this proposed optimization design technique, the development process, disposal technique and product formulation is optimized simultaneously to improve production profit, product behavior and disposal emissions. This “cradle to grave” optimization approach allowed a complex product formulation development process to be drastically simplified. The utilization of these modeling techniques took an industrial idea to full scale testing and production in under 18 months by reducing the number of subsequent laboratory trials required to optimize the formula, production and waste treatment aspects of the product simultaneously.

This particular development material involves the use of a polymer matrix that is applied to surfaces as part of a decontamination system. The polymer coating serves to initially “fix” the contaminants in place for detection and ultimate elimination. Upon mechanical entrapment and removal, the polymer coating containing the radioactive isotopes can be dissolved in a solvent processor, where separation of the radioactive metallic particles can take place. Ultimately, only the collection of divided solids should be disposed of as nuclear waste. This creates an attractive alternative to direct land filling or incineration. This philosophy also provides waste generators a way to significantly reduce waste and associated costs, and help meet regulatory, safety and environmental requirements.

In order for the polymeric film exhibit the desired performance, a combination of discrete constraints must be fulfilled. These interacting characteristics include the choice of polymer used for construction, drying time, storage constraints, decontamination ability, removal behavior, application process, coating strength and dissolvability processes. Identification of an optimized formulation that is suitable for this entire decontamination system requires integration of all the interlacing characteristics of the coating composition that affect the film behavior.

A novel systematic method for developing quantitative values for theses qualitative characteristics is being developed in order to simultaneously optimize the design formulation subject to the discrete product specifications. This synthesis procedure encompasses intrinsic characteristics vital to successful product development, which allows for implementation of the derived model optimizations to operate independent of the polymer film application. This contribution illustrates the optimized synthesis example by which a large range of polymeric compounds and mixtures can be completed.

Style manual or journal used: The American Institute of Chemical Engineering.

Computer Software used: Microsoft Word 2003, Microsoft Excel 2003, Microsoft Powerpoint 2003, TKSolver, Polymath, Maple, Visual Basic Applied.

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CHAPTER 1 INTRODUCTION OF THE OREX POLYMER STRIPPABLE FILM PROJECT FOR NUCLEAR POWER PLANT RADIOACTIVE DECONTAMINATION AND WASTE REDUCTION.

In the pages to follow, it will be shown that this project is a successful example of:

1) The integration of academic investigation and technology with industrial know-how and productivity.
2) Innovative model development techniques and “cradle to grave” optimization.
3) Novel waste management processing and waste reduction.

In order to illustrate these successes, an understanding of the project’s conception is required. The two major organizations that came together to develop this research consists of an academic consulting group and an industrial technology institution.

1.1 Auburn Engineering Technical Assistance Program. (AETAP)

The Auburn Engineering Technical Assistance Program (AETAP) is a National Science Foundation funded project consisting of a coalition of Samuel Ginn College of Engineering departments partnering with Alabama Cooperative Extension System (ACES), College of Business and other research and government establishments which focus on the needs of Alabama 's manufacturers. The primary objective of AETAP is to facilitate the transformation of knowledge from Auburn University into innovations that will create new wealth and strengthen Alabama's economy. AETAP provides manufacturers with high quality technical assistance, technology transfer, and workforce training. A knowledge sharing system based on the latest information technology is being used to expedite technology transfer. Students, faculty and county technology outreach agents use the system to transfer knowledge from Auburn and federal research laboratories to Alabama industry in a systematic manner. Thereby, AETAP helps increase Alabama's manufacturers competitiveness in a rapidly changing world of international commerce.

1.2 Orex Technologies, Incorporated.

Orex Technologies, Inc. produces and sells disposable polymer products such as protective clothing, gloves, booties and specialty items for the nuclear power industry. They are taking part in an ongoing partnership with the AETAP program with continued financial support for research and development of new polymer based products. In this research, effective and systematic models are devised to synthesize the optimal formulations for explicit engineering applications in the nuclear industry, i.e. radioactive decontamination and waste reduction. The major work of this partnership involves the use of a polymer matrix that is applied to surfaces as part of a decontamination system. The polymer coating serves to initially "fix" the contaminants in place for detection and ultimate elimination. Upon mechanical entrapment and removal, the polymer coating containing the radioactive isotopes can be dissolved in a solvent processor, where separation of the radioactive metallic particles can take place. Ultimately, only the collection of divided solids must be disposed of as nuclear waste. The outcome of this research opportunity creates an attractive alternative to direct land filling or incineration by conducting testing and optimization of the disposal process equipment. This philosophy also provides waste generators a way to significantly reduce waste and associated costs, and help meet regulatory, safety and environmental requirements.

1.3 Industrial Project Niche.

Exposures to particulate contaminants inside nuclear power plant refueling pools can contribute to health hazards, slower outage repair times, and play a role to overall plant contamination. In order to develop a model to predict the particle movement inside the reactor area, an understanding of the interior environment and standard operating procedures is required. A schematic of a standard refueling facility is shown in Figure 1.3-1. The reactor area itself is comprised of an enclosure that houses the plant floor spaces and the reactor refueling pool. This stainless steal pool is recessed into the ground beneath the plant floor. The nuclear reactor core is located at the base of this refueling pool along with the conveyor equipment required to move fuel rods in and out of the installation.

Under normal plant operation, this refueling pool is at a filled level even with the plant floor, however during the refueling process, this pool is drained and refilled a number of times in order to fulfill its role as barrier between the fuel rods and the containment air environment. The first of these draining steps is to allow human access to the head of the nuclear reactor. Technicians enter the refueling pool and dislodge the reactor head and attach a cable system to the vessel to allow for access to the fuel rods.

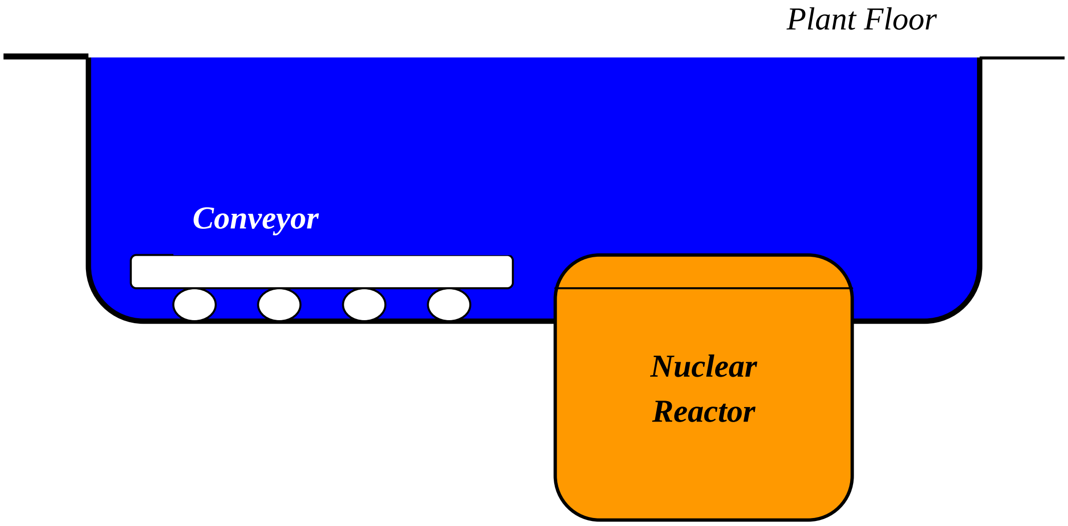

Figure 1.3-1 Nuclear Reactor Refueling Pool Schematic.

The pool is then refilled and the crane lifts the top of the reactor from the housing in the base of the refueling pool. The spent fuel rods are lifted out of the reactor and are removed from the refueling pool by a conveyer system, through special corridor in the pool wall and underground to another containment area for preparation for disposal. New fuel rods are also brought into the reactor containment area by this system of machinery. It is during this stage that the pool water is in direct contact with the enriched solid fuel and the radioactive contaminates are released. The reactor head is lowered back onto the vessel housing and the water is again drained to allow the technicians to reattach the top of the reactor and conduct any necessary maintenance. After the reactor outage maintenance procedures are completed, the refueling pool is refilled for the final time until the next scheduled refueling.

In this work, models for the route of dispersion and fate of particles within the interior of an enclosure are evaluated in order to analyze the concentration of aerosol contaminants. Concentration gradients occur when a contaminant is distributed unevenly throughout an enclosure. With a complex array of influences it is important to determine the mechanism dominating the transport and dispersion of indoor aerosols so that a complete understanding of the contamination phenomena is reached in order to develop practical engineering solutions to the contamination difficulty.

The migration of metallic constituents is studied by investigating the forces that act on single particles to determine the overall flux rates from the surfaces to the turbulent flow regions. The drag force, gravity, and Saftman lift forces are evaluated in the equation of motion to develop a dynamic model for particle transport. The influence of human activity is also investigated to determine a maximum aerosol concentration. These mathematical models will be used in the study to examine the possible dangers of the air born contamination problem seen during refueling operations in the nuclear power industry and provide a valuable understanding of viable solutions.

1.4 Model Development.

In order to compute realistic particle trajectories from an equation of motion, one needs to know the aero-dynamical forces acting on the system. The most important of these correlations are the lift and drag forces. It will be shown that most theoretical and experimental expressions for these forces are valid for a single spherical particle in an unbounded flow. Much less is known for these forces for the case of a particle in the vicinity of a solid surface, which is relevant for both the suspension and deposition portions of the model for the desired refueling pool study. In order to track the movement of the metallic particles through the air phase, the model is divided into separate transport phenomena; the removal rate of solids from the refueling pool walls into an air borne suspension and the transport of aerosol particles in the internal air currents. It is assumed that these phenomena occur in a two-layer model similar to deposition in Newtonian fluids, which is expressed by Thibodeaux (1996). The conditions by which this investigation is carried out make this an acceptable assumption because the removal of the contaminant from the wall occurs in a viscous sub-layer where laminar flows are present. The overall movement and fate of the particles takes place in the larger turbulent regions of the enclosure created by ventilation air movements. An example of a velocity profile at the junction two perpendicular surfaces is shown in Figure 1.4-1, which was presented by Brooke et.al. (1992).

1.4.1 Particle Velocity and Lift Force Model Analysis.

The models examined to determine the flux of particles from the pool surface into the air is derived from the analysis of the forces acting on single particles and is presented in a work of review notes by Hanratty. This investigation is restricted to a spherical particle that is small enough to be fully immersed in the viscous sub-layer. One of the earliest solid spherical particle equations of motion was derived through a number of different works from Basset, Boussing, and Oseen. The result of these works is the BBO equation.

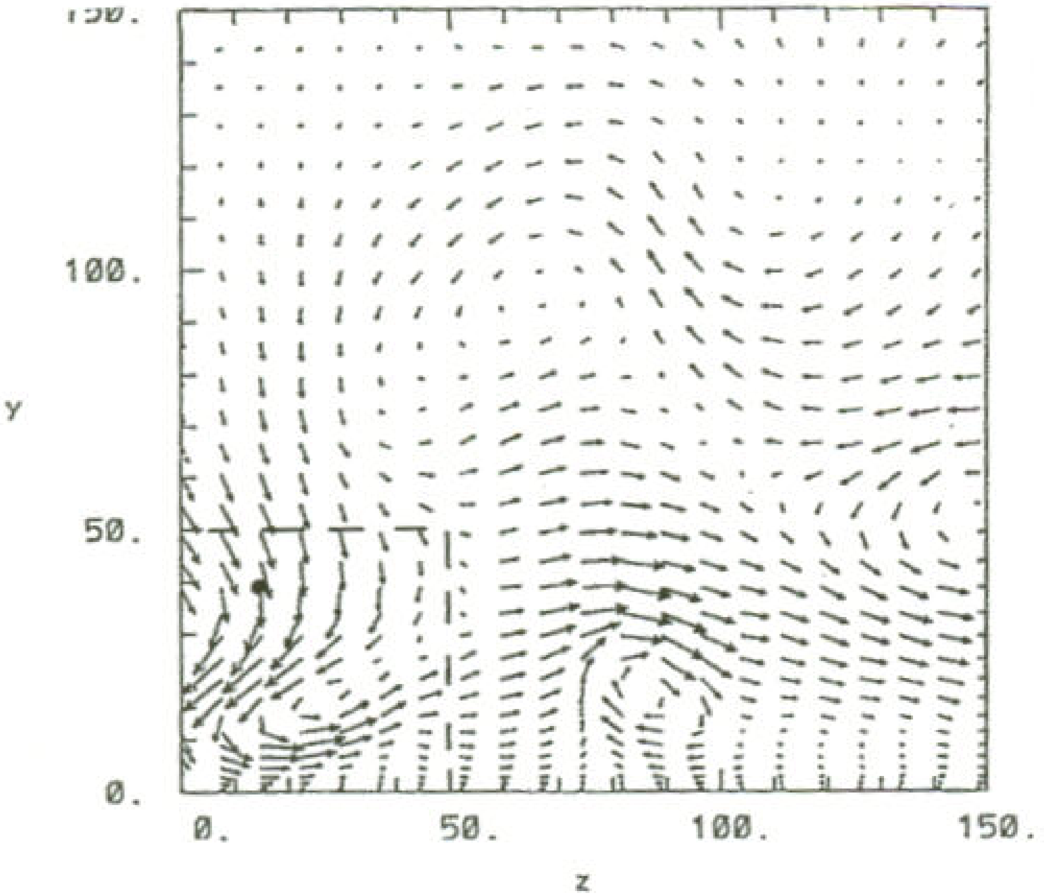

Figure 1.4-1 Instantaneous Velocity Profile at the Junction of Two Perpendicular Surfaces.

A sphere of radius a and density ρ_p, is moving in a Newtonian fluid of viscosity μ and density ρ_f. The aerosols are assumed to be small, rigid, spherical particles. The velocity of the particle is given in Equation 1.4-1.

Equation 1.4-1
$$m_p \frac{d\vec{V}_p}{dt} = -6\pi\mu a V_p(t) \; - 6\pi\mu a \frac{a}{\sqrt{\pi\nu}} \int_0^t \frac{dV_p}{ds} \frac{1}{\sqrt{t-s}} ds - \frac{2}{3}\pi\rho_f a^3 \frac{dV_p}{dt}$$

The first term of this equation is a pseudo steady-state Stokes drag force. The second term is called the Basset memory integral and takes into account the past actions of the particle. The third expression is an added mass term that accounts for the extra force required to displace the particle volume of the quiescent surrounding fluid. The limitation of this equation is the assumption that the disturbance due to the particle satisfies the Stokes flow equations, which is primarily used in laminar flow situations. Maxey and Riley (1983) propose a more generalized equation of motion where the solid particle can also be modeled in turbulent flow regimes that have larger Reynolds numbers. This velocity profile is shown in Equation 1.4-2.

Equation 1.4-2

$$\begin{aligned} \frac{dV_p}{dt} &= \frac{2(\rho-1)}{(2\rho+1)}g + \frac{2}{2\rho+1}\left(\frac{DV_f}{Dt} + \frac{1dV_f}{2dt} + \frac{a^2}{20}\frac{d\nabla^2 V_f}{dt}\right) \\ &\quad - \frac{9/(a^2\,\mathrm{Re})}{2\rho+1}\left(V_p - V_f - \frac{a^2}{6}\nabla^2 V_f\right) \\ &\quad - \frac{9/(a\sqrt{\pi}\,\mathrm{Re})}{2\rho+1}\int_0^t \frac{(d/dt)[V_p - V_f - (a^2/6)\nabla^2 V_f]}{\sqrt{t-\tau}}\,d\tau \end{aligned}$$

All of the physical quantities in Equation 1.4-2 are nondimensional and based in terms of wall units, which are rooted in the model intrinsic properties. (i.e. kinematic viscosity, friction velocity, density of fluid). The variable a is the particle radius, ρ is the ratio of particle density to the fluid density and g is the acceleration due to gravity. The variable V_p and V_f represent the velocities of the particle and fluid, respectfully. The first term in Equation 1.4-2 is the effects of the gravity force on the velocity of the sphere. The second is an added mass that accounts for the liquid displacement, which is similar to the third correlation in Equation 1.4-1. In Maxey and Riley's added mass term, the symbol D/DT denotes a time derivative using the undisturbed fluid velocity as the convective velocity. The third term of Equation 1.4-2 is a consideration of the Stokes drag forces hindering the movement of the particle, which is a function of both particle and fluid velocity. The final term is the Basset memory integral where the symbol d/dt signifies the time derivative following the sphere. The symbol τ is denoted as the dimensionless particle relaxation time.

Equation 1.4-3
$$\tau = [(2\rho + 1)/9]a^2$$

The fluid velocity profile can be obtained by numerically solving the Navier-Stokes equation:

Equaiton 1.4-4
$$\frac{\partial V_f}{\partial t} = -V_f \bullet \nabla V_f - \nabla p + \nabla^2 V_f + g e_1$$

where e_1 is a unit vector in the x-direction, g is the acceleration of gravity, and p is the pressure. The fluid is assumed to be incompressible which allows the assumption that $\nabla \bullet V_f = 0$. A more in depth derivation of this model is given by Brooke et. al. (1992). Because the particle size is very small and the fluid in question is air with a density much small than that of the particle, the contributions of the Basset history integral and added mass can be neglected from the motion of the particle. With this simplification made by Zhang and Bogy (1997) the particle motion equations can be written as

Equation 1.4-5
$$\frac{dX_p}{dt} = V_p$$

Equation 1.4-6 $$m_p \frac{dV_p}{dt} = F_D + F_l + F_g$$

where m_p is the mass of the particle, X_p and V_p are the position and velocity vectors of the particle in an air bearing, F_D, F_l and F_g are respectively the forces of drag, lift and gravity.

1.4.1.1 The Drag Force.

For a rigid sphere moving in an airflow, the drag force can be expressed as

Equation 1.4-7 $$F_D = \frac{\pi}{8} C_D \rho_f d^2 \left| V_f - V_p \right| (V_f - V_p)$$

where C_D is the drag coefficient, d is the diameter of the sphere, ρ_g is the density of the air and V_f is the velocity of the "fluid" gas phase. The approach implemented to calculate the drag coefficient for small particles is to use the theory of gas dynamics and is outlined in works by Zhang and Bogy (1997).

1.4.1.2 The Lift Force.

For the model development constraints in this work, the BBO and Maxey/Riley models are valid only in areas far from the recessed walls of the refueling pool. Neither of these equations accounts for the affects of the walls on the particle. A number of solutions have been developed to account for these different wall effects and the manner in which the force contributions in Equation 1.4-5 are calculated. Brenner (1961) develops a model that accounts for the drag on a particle that is moving perpendicular to the floor. However, his proposed modified Stokes drag coefficient diverges as the sphere approaches the wall. This model is not effective for analyzing the aerosol suspension in refueling pools, but it does show that the effects of the wall must be considered. Likewise, Goldmax et. al. (1967) account for this interaction by considering the forces on a solid sphere translating parallel to the wall. Separate correlations are tabulated to determine the translational, rotational and shear stress in both the turbulent and viscous regions. The drag effect and velocity profile can be estimated by this work, but in the current refueling pool situation, the particles in contact with the surfaces and are initially at rest. An estimation of the lift forces in the viscous sub-layer must be considered. The most notable study to address this type of lift force was conducted by Saftman (1965). The shear lift forces caused by the movement of the air around the particle in a turbulent manner are introduced with a term known as Saftman lift. This force acts in the direction perpendicular to the motion of the particle. In the absence of the particles in the air current, the flow field is given as

Equation 1.4-8 $$\vec{V}_f = G_x \hat{z}$$

where G_x is the velocity gradient in the x direction. Similarly, the velocity of the sphere is shown in Equation 1.4-9.

Equation 1.4-9 $$\vec{V}_p = (G_x - v_s)\hat{z}$$

The v_s term accounts for the slip of the particle in the flow field. This slip velocity consideration is considered positive if the particle lags the air stream and negative if the sphere leads the surrounding flow. By assuming that the Reynolds numbers associated with slip velocity (Re_s), gravity velocity (Re_g) and shear velocity (Re_Ω) are all considerably smaller than 1, Saftman determined that the lift force on a rotating sphere in the x direction is estimated as

Equation 1.4-10
$$F_l = 6.46 a\mu V_s \sqrt{\mathrm{Re}_g} + \frac{\pi}{2} a\mu V_s \mathrm{Re}_\Omega - \frac{11\pi}{16} a\mu V_s \mathrm{Re}_g$$

This solution was later revisited in a number of subsequent works. In these efforts, the assumption of $\sqrt{Re_g} >> Re_s$ that allows for the development of the correlation in Equation 1.4-7 possible is re-evaluated. In large enough turbulent flows, this assumption can be violated. McLaughlin (1993) proposed that the lift force is more closely approximated with the expression in Equation 1.4-11.

Equation 1.4-11
$$F_l = 6.46 a\mu V_s \sqrt{\mathrm{Re}_g} \left(\frac{J(\varepsilon)}{2.255}\right)$$

The ε term is the ratio of the $\sqrt{Reg}$ to Res. This estimation was expanded to include corrections to account for wall effects, where J_w is a wall modification term and J_u is the unbounded lift modification seen in Equation 1.4-12.

Equation 1.4-12
$$F_l = 6.46 a\mu V_s \sqrt{\mathrm{Re}_g} \left(\frac{J_u(\varepsilon) + J_w(\varepsilon)}{2.255}\right)$$

Cox and Hsu (1977) also derived lift approximations that included wall induced lift effects as well as rotational correlations. Because the particles in the refueling pool are in contact with the surfaces, it is assumed that the frictional forces associated with the contact will initially prohibited particle rotation. This lack of rotation must be assumed to occur everywhere in the viscous sub-layer of the refueling pool model. The Cox and Hsu lift equation for a non-rotating sphere in a laminar flow is expressed in Equation 1.4-13. This model is an exact analytical expression that includes a wall induced lift term, shear stress effect from the wall term and a shear stress effect from the fluid, respectfully. The distance from the solid surface to the sphere is denoted as l.

Equation 1.4-13

$$F_l = \frac{9\pi}{16} a^2 V_s^2 \rho + \frac{33\pi}{32} G a^2 V_s \rho l + \frac{366\pi}{576} \rho a^4 G^2$$

A true estimation of the lift on a particle from airflow movement must be derived in order to determine the flux rate of particle from the surfaces to the indoor atmosphere of the refueling pool. The work of Leighton and Acrivos (1985) was investigated in order to fulfill this specification. It is determined that the lift on a sphere in contact with a surface is modeled by Equation 1.4-14 and shown in Figure 1.4-2. The forces acting on the particle are shown as F_l for the lift, F_D for the drag and F_g for the gravity.

In this representation of lift, the term G refers to the velocity gradient of the fluid, a is the radius of the particle, μ and ρ are the viscosity and density of the fluid, respectfully.

Equation 1.4-14

$$F_l = 9.22 \frac{\pi G^2 a^4 \mu^2}{\rho}$$

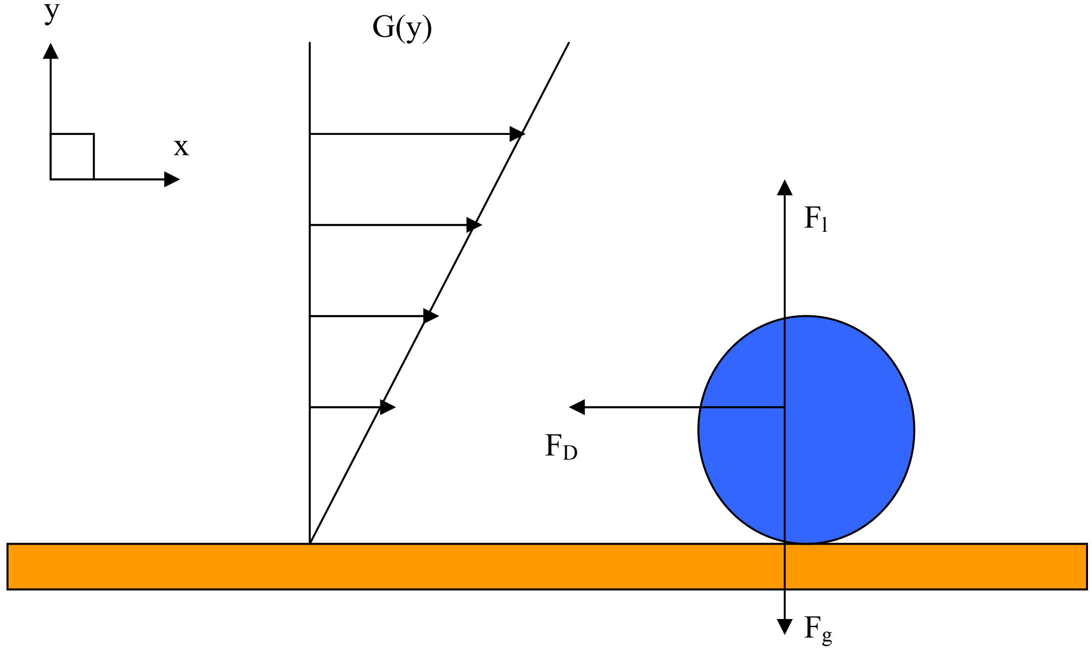

Figure 1.4-2 Forces Acting on a Particle on the Wall Due to the Velocity Gradient in the Viscous Sub-layer.

This model is restricted to a particle that is small enough to be fully immersed in the viscous sub-layer. The correlation is the best estimate of the lift forces induced on a spherical particle inside the depths of a nuclear power plant refueling pool.

1.4.1.3 The Gravity Force.

Gravity force is related to the occupied space by the sphere itself. Since its magnitude is proportional to the third power of the diameter of the sphere, it is much smaller than the magnitude of the drag in the same direction, so its components in the other two directions can be neglected. This is expressed as

Equation 1.4-15
$$F_g = \frac{\pi}{6} d^3 (\rho_g - \rho_p) g_y$$

With this final derivation, Equation 1.4-6 is completed by substitution of Equation 1.4-7, 1.4-14, and 1.4-15. However, this model is not adequate because it is necessary to derive the correlation to relate the single particle forces to an overall net flux of particles leaving the surfaces to the air phase. The particles that redeposit onto the surface must also be considered. Ultimately, it is desired to determine the concentration of the aerosol in the air of the containment enclosure. At this juncture, it has been shown that the flux rate of contaminate from airflow velocity and particle forces consists of three major contributions… Drag, Lift and Gravity. Specific assumptions must be considered in order to develop an accurate model to simulate the aerosol contaminate behavior inside the refueling pool region before possible solutions to the phenomena can be tested.

1.4.2 Refueling Pool Assumptions.

Upon consideration of the magnitude of the proposed lift forces, it can be concluded that the majority of airborne contaminates in the refueling pool case study are traced back to human interaction. The forces of gravity and friction that hold the particles in place on the pool surfaces are easily overcome by outside influences. In an investigation of aerosol concentration by Roshanaei and Braaten (1996), this assumption is validated. Figure 1.4-3 illustrates how human and machine action increases the suspension rate of particulate.

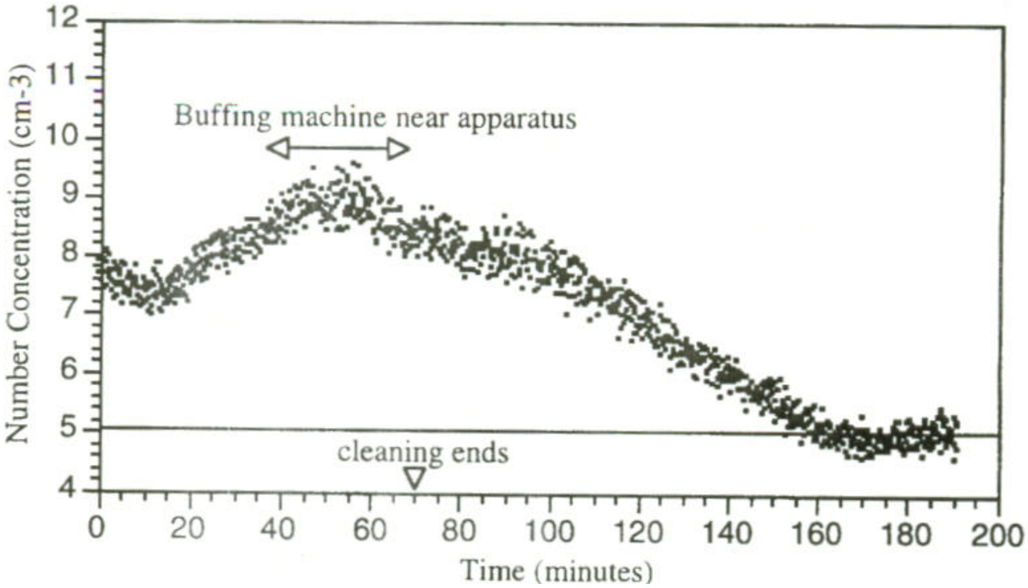

Figure 1.4-3 Aerosol Concentration During and After a Scheduled Cleaning Cycle of an Enclosed Area. *Thatcher and Layton (1995)*

1.4.3 Mechanical Resuspension Models.

In order to model a suspension rate in the refueling pool, it is necessary to assume that mechanical interaction is the main driving force in the suspension process. A model that accounts for this effect is presented to characterize indoor resuspension by Thatcher and Layton (1995). This work affirms the observation that particle resuspension by human activities such as cleaning or walking are an important factors in indoor particle concentration. The effect of particulate concentration outside of the enclosure is also studied in the work. The proposed steady-state model is shown in Equation 1.4-16 where C_{in} is the concentration of particles in the indoor air (mg/m^3), L_{fl} is the mass loading of particles on accessible surfaces (mg/m^2), A_{fl} is the surface area of the exposed surfaces (m^2), R is the resuspension rate of particles from the surface (1/h), λ_v is the air exchange rate (1/h), C_o is the concentration of particles in the outside air from the enclosure (mg/m^3), P is the fraction of outside particles that penetrate the enclosure (dimensionless), V is the volume of the control enclosure (m^3), G is the indoor particle generation rate (mg/hr), A_d is the surface area for particle deposition (m^2), and V_d is the deposition velocity (m/h).

Equation 1.4-16 $$C_{in} = \frac{L_{f1}A_{f1}R + \lambda_v PVC_O + G}{A_d V_d + \lambda_v V}$$

A number of these values must be determined experimentally as well and analytically. The experimental correlation of the infiltration air exchange rate is determined to be

Equation 1.4-17 $$\lambda_v = \frac{1}{(t - t_{o)}} \ln(\frac{C}{C_O})$$

where C_O is the initial concentration of a tracer gas and C is the concentration present after the time interval (t-t_o). Exfiltration and deposition are the only major losses of indoor particles. The gain from infiltraton is minor since the concentration outside the control volume is much lower than the inside air. The deposition loss rate can be calculated using the following equation:

Equation 1.4-18 $$\lambda_d = (\frac{1}{t}) \ln(\frac{C_i}{C}) - \lambda_v$$

where C_i is the initial concentration of suspended particles (particles/m^3), C is the final concentration of suspended particles (particles/m^3) and t is the time between measurement C_i and C(h). From this value the deposition velocity can be estimated. It is shown in Equation 1.4-19.

Equation 1.4-19
$$V_d = \frac{\lambda_d V}{A_d}$$

The penetration factor must also be determined in order to use the model proposed in Equation 1.4-16. However, in one of the conclusions of the work of Thatcher and Layton, it was determined that penetration factor can be eliminated as a model parameter without any loss of accuracy because the indoor enclosure provides little filtration of airborne particles present in the ambient air. By neglecting this parameter and assuming that there is no particle generation, Equation 1.4-16 is simplified and rearranged to find the resuspension rate, R.

Equation 1.4-20
$$R = \frac{C_{in}(A_d V_d + \lambda_v V) - C_O \lambda_V V}{L_{f1} A_{f1}}$$

The mass of material resuspended is proportional to the amount of material available for resuspension on the surfaces of the enclosure. The manner in which this resuspension rate is determined accounts for human interaction and particle size. Examples of these values are found experimentally and are reported in Table 1.4-1. The values of deposition velocity are also detailed in Table 1.4-2.

By using these tabulated values a concentration estimate of particulate in the refueling pool can be determined. These tables do not differentiate between different levels of disturbance. The amount of activity that occurs during the refueling outage is much greater than the constraints that were used to estimate the resuspension rate or deposition velocities. The effect of this increased activity can be seen in the work of Karlsson et.al.(1999) where an increasing activity level was studied. Figure 1.4-4 shows this increased resuspension effect.

Table 1.4-1 Experimental Values for Particle Loss Rate, Deposition Loss Rate and Deposition Velocity.

Karlsson et.al.(1999)

Sample Date	Particle Size Range (μm)	Overall Particle Loss Rate (h^{-1})	Air Infiltration Rate (h^{-1})	Particle Deposition Loss Rate (h^{-1})	Deposition Velocity (m/h)
7/22/1993	1--2	0.55	0.30	0.25	0.60
	2--3	0.85	0.30	0.55	1.32
	3--4	1.07	0.30	0.77	1.85
	4--6	1.98	0.30	1.68	4.03
7/23/1993	1--2	0.46	0.18	0.28	0.67
	2--3	0.93	0.18	0.75	1.80
	3--4	1.02	0.18	0.84	2.02
	4--6	1.96	0.18	1.78	4.27
8/10/1993	1--2	0.60	0.14	0.46	1.10
	2--3	1.50	0.14	1.36	3.26
	3--4	2.50	0.14	2.36	5.66
	4--6	1.20	0.14	4.06	9.74

Table 1.4-2 Experimental Resuspension Rates for 4 persons at Normal Activity Rates.

Karlsson et.al.(1999)

Particle Size Range (μm)	Indoor Particle Concentration (μg/m^3)	Indoor Particle Concentration (μg/m^3)	Particle Deposition Loss Rate (h^{-1})	Air Infiltration Rate (h^{-1})	Resuspension Rate (h^{-1})
0.3--0.5	1.2	0.3	0.0	0.3	9.9×10^{-7}
0.5--1	0.5	0.1	0.0	0.3	4.4×10^{-7}
1--5	6.8	3.0	0.5	0.3	1.8×10^{-5}
5--10	14.3	10.9	1.4	0.3	8.3×10^{-5}
10--25	38.0	21.7	2.4	0.3	3.8×10^{-4}
>25	2.0	1.4	4.1	0.3	3.4×10^{-5}

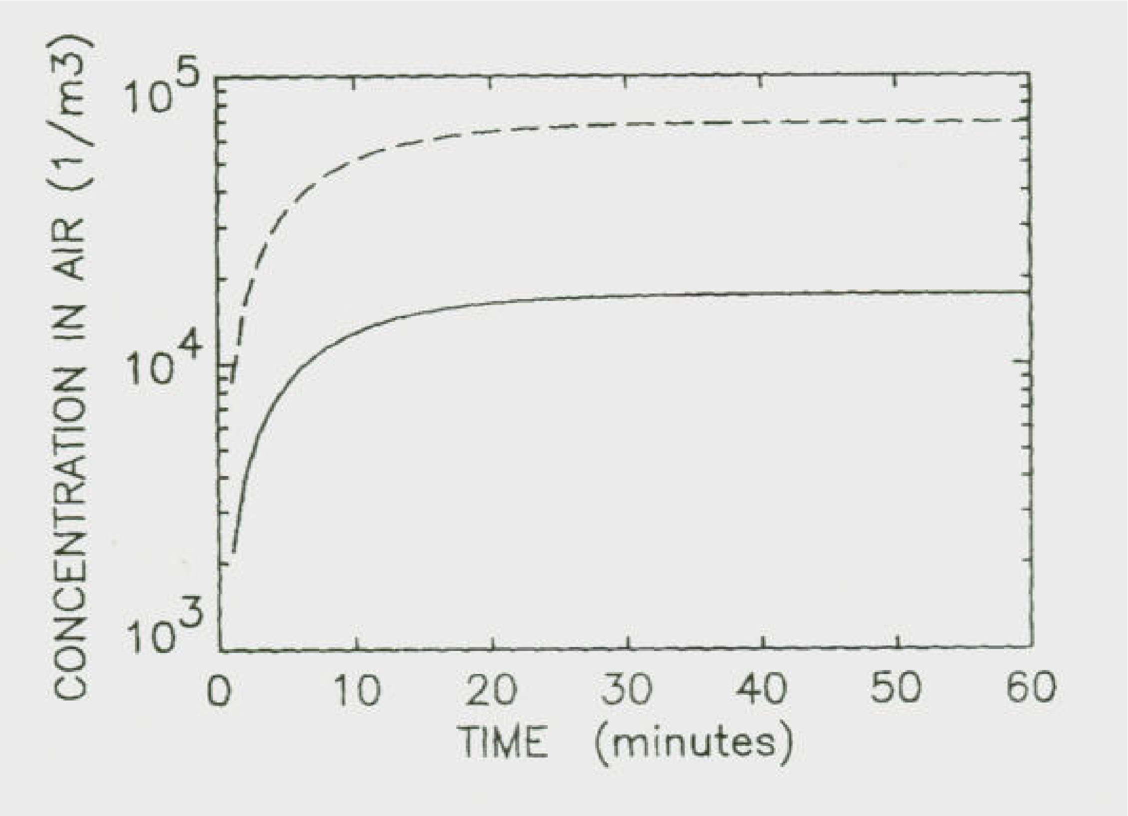

Figure 1.4-4 Example of Model Calculated for the Effect of the Actions of 1 and 4 persons. *Karlsson et.al.(1999)*

This data leads to the development of a dynamic model that determines the number of particles emitted by human activity as well as develop a dynamic concentration profile of the enclosed control volume. This model is comprised of the following equations.

Equation 1.4-21
$$\frac{dm_j}{dt} = V_{dj}C_i - \frac{r_{ja}m_jA_a\Lambda_{aj}}{A_j} - \gamma_s m_j$$

Equation 1.4-22
$$\frac{dC_i}{dt} = kC_O(1-f_O) - kC_i - \sum_j^N (A_j/V) V_{dj} C_i + \sum_j^N \frac{r_{ja} m_j A_a \Lambda_{ja}}{V} - \gamma_a C_i - (V_{ei}/V) f_i C_i$$

In the work of Karlsson et. al.(1999) a resuspension model is formulated and based on a non-dimensional parameter denoted the resuspension fraction, r_{ja} and the frequency of human activity. This resuspension fraction is defined as the fraction of particles emitted from the contact area, A_a (m^2). An example of the contact area is the area of the sole and heel of one shoe during one cycle of activity such as one-foot step. The control volume enclosure is assumed to be well mixed in the development of Equation 1.4-21 and Equation 1.4-22. m_j is the mean number of particles per unit area on a surface j (particles/m^2), V_{dj} is the deposition velocity (m/s) to surface j, and C_i is the indoor concentration (particles/m^3). Λ_{ja} is the contact frequency, which is defined as the frequency of contacts between the persons and the surface. An example of this is the number of foot steps per second. C_O is the concentration of aerosol outside the control volume (particles/m3), f_O is the external filter factor (non-dimensional), k is the air exchange rate (1/s), A_j is the total indoor surface areas with orientation j (m^2), N is the number of orientations of the surfaces, V is the room volume (m^3), γ_s is the decay rate and the surface (1/s), γ_a is the depostion rate (1/s), V_{ei} is the flow of internal filtration (m^3/s), and f_i is the internal filter factor (non-demsional) which is the fraction of aerosols removed by aerosol filters such as lungs or filtration equipment.

The concentration in the air, C_i, and the resuspension fraction, r_{ja}, were calculated from the deposited number of particles using an irrelative method to solve Equation 1.4-

21 and Equation 1.4-22. The experiments of Karlsson et.al. (1999) resulted in similar values of r_{ja} independent of contact frequencies Λ_{ja}, thus verifying the resuspension formulation of these equations. These modeling equations are to be used in the investigation of aerosol concentrations in the nuclear power plant refueling pool case study.

1.4.4 Model Application.

In order to develop a suitable adaptation of Equation 1.4-21 and Equation 1.4-22 for the particular case study under review, it is necessary to define and determine suitable values for the constituent model parameters. The required measurements are detailed in Figure 1.4-5.

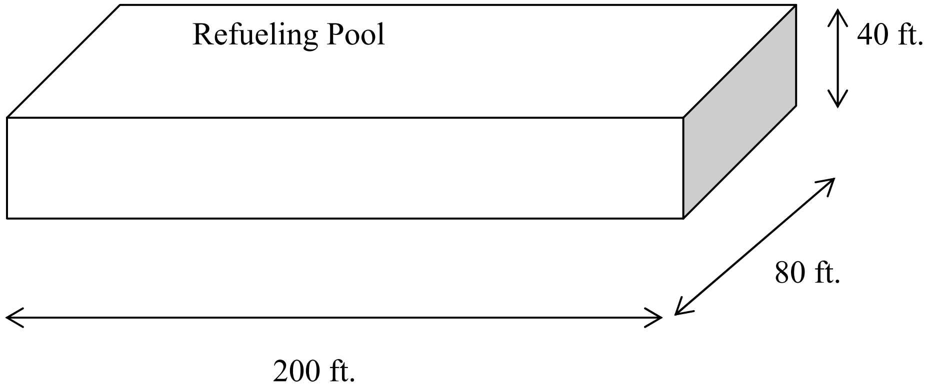

Figure 1.4-5 Dimension Schematic of a Typical Nuclear Power Plant Refueling Pool.

Table 1.4-3 Computer Simulation Variable Values for a Nuclear Refueling Pool Scenario.

Variable	Description	Value	Reference
V_{dj}	depostion velocity	4.03	Table 1.4-1.
R_{ja}	resuspension factor	5×10^{-4}	Determined experimentally by Karlsson et.al.
A_a	contact area	$.028\text{m}^2$	Average surface area of one shoe.
Λ_{aj}	contact frequency	300 steps/min.	Assuming 4 persons at average walking pace.
A_j	total indoor area	16000ft^2	Horizontal floor surface from Figure 1.4-5.
γ_s	decay rate at the surface	1.98/h	Table 1.4-1.
k	air exchange rate	.5/h	Karlsson et.al.
C_O	outside aerosol concentration	0	Assuming outside air is free of contaminate and well mixed.
f_O	external filter factor	------	Because $C_O = 0$, value is not necessary.
V	volume	$1.28 \times 10^5\text{ft}^3$	Figure 1.4-5.
γ_a	decay rate of the air	1.68/h	Table 1.4-2.
V_{ei}	flow of internal filtration	0	In order to determine the maximum contaminate concentration, assumed to be 0.
f_j	internal filter factor	-------	Because $V_{ei} = 0$, value is not necessary.

With these assumptions in place, Equation 1.4-21 and 1.4-22 become

Equation 1.4-23
$$\frac{dm_j}{dt} = V_{dj}C_i - \frac{r_{ja}m_jA_a\Lambda_{aj}}{A_j} - \gamma_s m_j$$

Equation 1.4-24
$$\frac{dC_i}{dt} = -kC_i - \left({}^{A_j}\!/\!_{V}\right)V_{dj}C_i + \frac{r_{ja}m_jA_a\Lambda_{ja}}{V} - \gamma_a C_i$$

By attaining a value for the initial concentration of the particle contaminate on the surface of the refueling pool floor, this model can be solved analytically to find a concentration profile verses time after human activity in the recessed region. A computer generated simulation of this profile is given in Figure 1.4-6 using the same surface loading as Karlsson et. al. The information required to solve for a more accurate model must be conducted. The deposition velocities reported in Table 1.4-1 are for horizontal surfaces only. With further experimentation to derive deposition velocities and decay rates, the model can be expanded to include the vertical spaces of the pool region. At this time, estimated data is available for the horizontal floor region only.

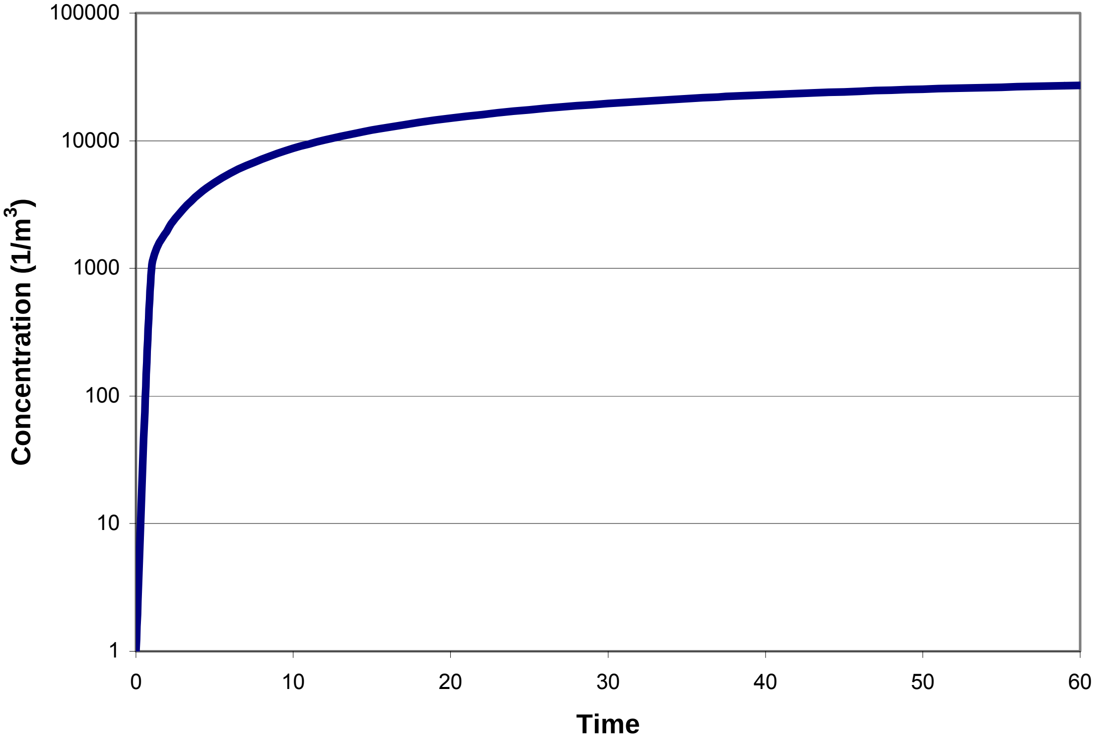

Figure 1.4-6 Simulated Aerosol Concentration in a Nuclear Power Plant Refueling Pool After Human Infiltration.

The steady state concentration of particles in the air of the recessed pool is illustrated by Figure 1.4-6 is slightly lower than that reported by Karlsson et.al. in Figure

1.4-4. This difference is on account of the room volume increase with the air exchange rate remaining constant.

This model is development to monitor the concentration of aerosol during human intervention only, a entire different simulation in the time region after human intervention would create a model similar to the actual behavior measured in Figure 1.4-4. this evaluation is concerned mainly with the maximum concentration and worst case scenarios and even though an extensive amount of simplification is conducted on the model, the data of the simulation exhibits an accurate pattern of the mass transport phenomena of radioactive particulate seen in nuclear reactor refueling pools. This adapted model developed by Karlsson et. al. gives rise to the discovery that a process addition or modification should occur prior to the human infiltration of the refueling pool in order to decrease the chances of particle disturbance and ultimate suspension. The model illustrates that once the contaminate reaches the aerosol phase, the concentration gradient from the refueling pool air to the ambient air of the entire enclosure causes a much larger containment deposition dilemma. The primary simulation conclusion is that a means to either stop or hinder this transport must be investigated and developed.

1.5 The “Cradle to Grave” Optimization Theory and Proof of Concept Analysis.

A novel method to develop a coating that can satisfy the industry niche discussed in the previous chapter sections must be created to find practicable formula solutions quickly and cost effectively.

The formula optimization of new products and improvement of existing merchandise is practiced in many different industries including paints and dyes, polymers and plastics, foods, personal care, detergents, pharmaceuticals and specialty chemical development. Current trends in the engineering design community have moved towards the development of quantitative integrated solution strategies for simultaneous consideration of multiple product characteristics. The optimization variables are most often determined by qualitative attributes, stochastic variables, visual observations and/or design experience. The effectiveness of these approaches is limited by available data, bias towards specific solutions and experimental error and reproducibility. Model insight is required for development of fast, reliable and systematic screening methods capable of identifying optimal formulations and reducing the number of subsequent laboratory experimentations.

In this work, an effective and systematic model is devised to synthesize the optimal formulation for an explicit engineering application in the nuclear industry, i.e. radioactive decontamination and waste reduction. This material development involves the use of a polymer matrix that is applied to surfaces as part of a decontamination system. The polymer coating serves to initially “fix” the contaminants in place for detection and ultimate elimination. Upon mechanical entrapment and removal, the polymer coating containing the radioactive isotopes can be dissolved in a solvent processor, where separation of the radioactive metallic particles can take place. Ultimately, only the collection of divided solids should be disposed of as nuclear waste. This creates an attractive alternative to direct land filling or incineration. This philosophy also provides waste generators a way to significantly reduce waste and associated costs, and help meet regulatory, safety and environmental requirements.

In order for the polymeric film exhibit the desired performance; a combination of discrete constraints must be fulfilled. These interacting characteristics include the choice of polymer used for construction, drying time, storage constraints, decontamination ability, removal behavior, application process, coating strength and dissolvability processes. Identification of an optimized formulation that is suitable for this entire decontamination system requires integration of all the interlacing characteristics of the coating composition that affect the film behavior.

A novel systematic method for developing quantitative values for theses qualitative characteristics is developed in order to simultaneously optimize the design formulation subject to the discrete product specifications, the process equipment parameters to the maximum profitability, and the removal methods to minimize environmental impacts. The predictive modeling framework developed for solving this integrated problem is comprised of material and energy balances, constraint parameters, constitutive equations, design/optimization variables, and overall “cradle to grave” limitations. Multiple combinations of user-defined design constraints generate different optimization objectives and thus may result in different formulations. This synthesis procedure encompasses intrinsic characteristics vital to successful product development, which allows for implementation of the derived model optimizations to operate independent of the polymer film application. This contribution illustrates the optimized synthesis by which a large range of polymeric compounds and mixtures can be completed.

1.5.1 Current Development Trends.

Typical product development and the associated processing systems in industry occur in three separate stages; formula creation, production design and waste management. Not only do different groups of chemists, engineers and scientists generally conduct these three stages of development, but also different companies and institutions. New products are formulated in laboratory experiments to improve on existing industrial niches or to create completely new markets. These formulas are optimized to produce the best possible product behavior in order maximize marketability. This product recipe is then passed on to the process development researchers to determine the optimized manufacturing system of equipment, chemistry and fabrication methods. It's not uncommon to outsource production to entirely different companies, with can separate the goals of product creation and process equipment usage. Even though this network of equipment is also optimized with consideration to production rate, manufacture efficiency and profitability, the optimized product train is limited to processes that only produce the independently optimized product formula. The combination of the product formulation and manufacturing process creates an entirely new system that must be optimized. Even though the formula and process are considered optimal, because they were determined independently from one another, the overall system may not be at the peak of working conditions. Because of non-linear chemistry, thermodynamics and mechanics, small changes in product formula may relate to drastic changes in the production requirements and vise versa. In the case of products that are not completely consumed or create byproducts, the waste and refuse processes creates another process associated with the formula. A separate company or institution generally conducts this process, whether it is water treatment, recycling, destruction, or land filling. As in the production process, small changes in the formula can create drastic changes in the waste management aspects of the product. These independent process optimizations are illustrated in Figure 1.5-1(a).

1.5.2 “Cradle to Grave” Optimization Theory.

In the hazardous material management and governmental regulation compliance fields, there is a concept known as “cradle to grave” liability for hazardous materials producers. This concept is a way of thinking created by current governmental regulations. The Resource Conservation and Recovery Act (RCRA) of 1976, which amended the Solid Waste Disposal Act, was the first substantial effort by Congress to establish a regulatory structure for the management of solid and hazardous wastes. This set of regulations yielded a complex assortment of regulations governing the management of hazardous waste from "cradle to grave". Specifically, Subtitle C of RCRA addresses this "cradle-to-grave" concept and the associated requirements for hazardous waste from the point of generation to disposal. Even though product formulation rarely has anything to do with hazardous material development, our optimization technique adopts a similar concept, optimizing all the product behaviors between development and disposal.

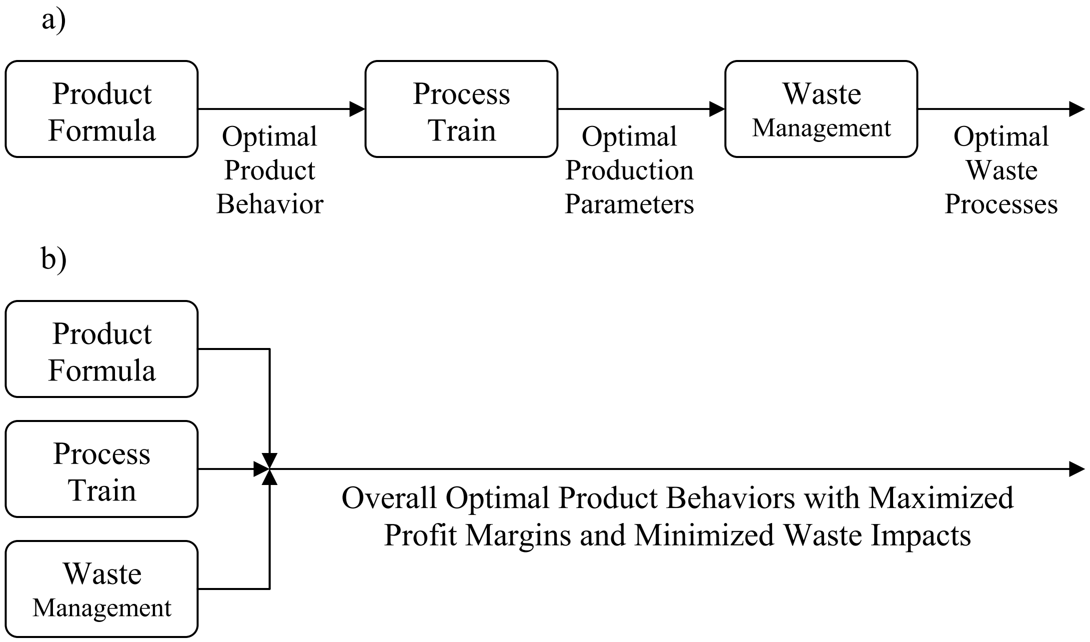

Figure 1.5-1 Process Optimization Techniques.
a) General Formula Development and Manufacturing Process Optimization Practice
b) Cradle to Grave Product Optimization

With the increasing pressure of reducing contaminate regulations of wastewater streams, new techniques of maintaining governmental compliance must be developed. By applying the concept of cradle to grave responsibility to product formulation, a reduction in measured effluent parameters can be achieved. This can possibly be accomplished by optimizing the product formulation and production process to reduce the amount of associated byproduct that must be disposed of. By optimizing the product formula, process parameters, and disposal procedures simultaneously, the entire system produces acceptable product behaviors, maximum manufacturing process profitability and efficiency, and minimum waste impacts and costs.

1.5.3 Proof of Concept Experimental Analysis.

Before the “cradle to grave” optimization theory can be applied, the basic behaviors of polyvinyl alcohol strippable coatings must be determined to experimentally discover if embedding the particle contaminate is feasible. In order to best illustrate these basic inherent product phenomena, four different formulations will be considered and compared to one another. This primary experimentation is required to determine what parameters must be optimized to develop a successful industry supported product. Each formulation is an example of the best combination of ingredients that expresses the specific behaviors vital to the process decontamination ability. This list of attributes includes different application techniques, solvent volatilities, shelf performances, and drying times. The experimental procedures and data analysis for determining these traits are illustrated in Appendixes C through F.

In order to express the properties of the different coatings, it is necessary to define concepts of the coating behavior and create a common language to properly compare the film properties.

CURING—The technical definition of curing implies a chemical reaction. An example of this concept is concrete. In our particular case, curing is best explained as an evaporation rate. The time required for the film to “cure” is the point where the coating has lost most of its tacky texture and wet appearance. When the coating has cured, an overcloth can be applied without extensive liquid absorption into the fabric and rubber mats may be laid down to protect the coating integrity from technician foot traffic.

DRY-THROUGH—This is a technical term used in the paint industry to illustrate the point when a paint or coating has lost all of the moisture/solvent that will be evaporated. The coating will always retain a certain amount of the solvent.

DRY TO TOUCH—This is the point in the coating curing when the overcloth can be applied. The film may still posses a slightly tacky texture, but does not leave any moisture or residue on the finger.

OVERCLOTH—This is the layer of polymer cloth that is applied over the coating once it has cured to an acceptable moisture content. This cloth acts as a barrier between the coating and the rubber mating that the crew walks on.

ELASTOMER—This is an additive used to molecularly separate polymer chains and reduce the amount of hydrogen bonding and interaction between polymer chains.

REANIMATION—This is a required process for coatings with high concentrations of polymer. After sitting at room temperature for times in excess of 36 hours, certain coating formulations settle into a "Jello-like" solid that cannot be efficiently pumped. In order to return this coating to a Newtonian fluid, it must go through a reanimation process which involves raising a mixture's temperature above the glass transition temperature of the polymer used.

1.5.3.1 Sample 4.

The composition of Sample 4 is a relative standard used throughout the duration of the project. This formula comprised of 20% polyvinyl alcohol, 5% glycerol, and 75% water is a recommended example of a film producing solution by the PVA manufacturer. This is the stock solution that was determined to establish a “proof of concept” to the industrial investors in the proposal stages of the project. It was included in this report to serve as a benchmark for the final formula selection process. It has been shown that it has no advantage over any other test sample and that the process properties have the potential to be more adequately optimized.

1.5.3.2 Sample 1.

This is primarily comprised of a polymeric backbone structure (polyvinyl alcohol), an elastomer additive (glycerol), a primary solvent (water), and a secondary solvent (ethanol). In comparison with the other samples, this formula is deficient in polymer and elastomer, but enriched in both primary and secondary solvents.

1.5.3.2.1 Advantages.

The purpose of this coating formulation was to create a coating that maintains liquid properties over long periods of time. The lack of a reanimation process simplifies the application technique. No special heaters, stirrers, or vessels are required. Because of this fact, the formula allows for the distribution of the coating in 5 or 10-gallon quantities, which is a desired product goal.

To study improvements on curing times, ethanol is added in place of excess water. Ethanol is more volatile than water and increases the evaporation rate of the overall solvent system and in turn reduces the curing time required for the film production. Because of this added volatility, tests were conducted to determine the safety of the coating in the presence of direct flame that could be produced from cutting and welding equipment. These bench top tests found that the coating would not flash or ignite when brought into contact with direct flame at room temperature (27 ^{o}C). If a product formulation similar to this sample is feasible for production, it is important to determine an open-cup flash point. This is a requirement of both Occupational Safety and Health Association (OSHA) and the Department of Transportation (DoT) regulations of any product that contains volatile substances. Any chemical compound that is stored on site or transported across roads or rail must have this testing completed in order to determine a hazardous classification. A description of this standardized test is outlined in Appendix C with the data generated from the testing.

The effect of adding the secondary solvent into the formulation can be illustrated in Figure 1.5-3. This graph illustrates the weight loss of the four coatings as a function of time. It is apparent that the rate of weight loss of coating Sample 1 is the best of the measured films. It should be noted, however that this phenomenon is counteracted by the fact that Sample 1 also contains the highest concentration of total solvent. It might in fact lose weight more quickly, but it contains more liquid to evaporate than the other coatings. Figure 1.5-4 illustrates the evaporation effect that the ethanol has on the curing process more clearly. Here the weight percents of only the solvent present in the liquid are taken into account by calculating mass balances on the evaporation process.

Figure 1.5-2 Coating Fluid Samples.

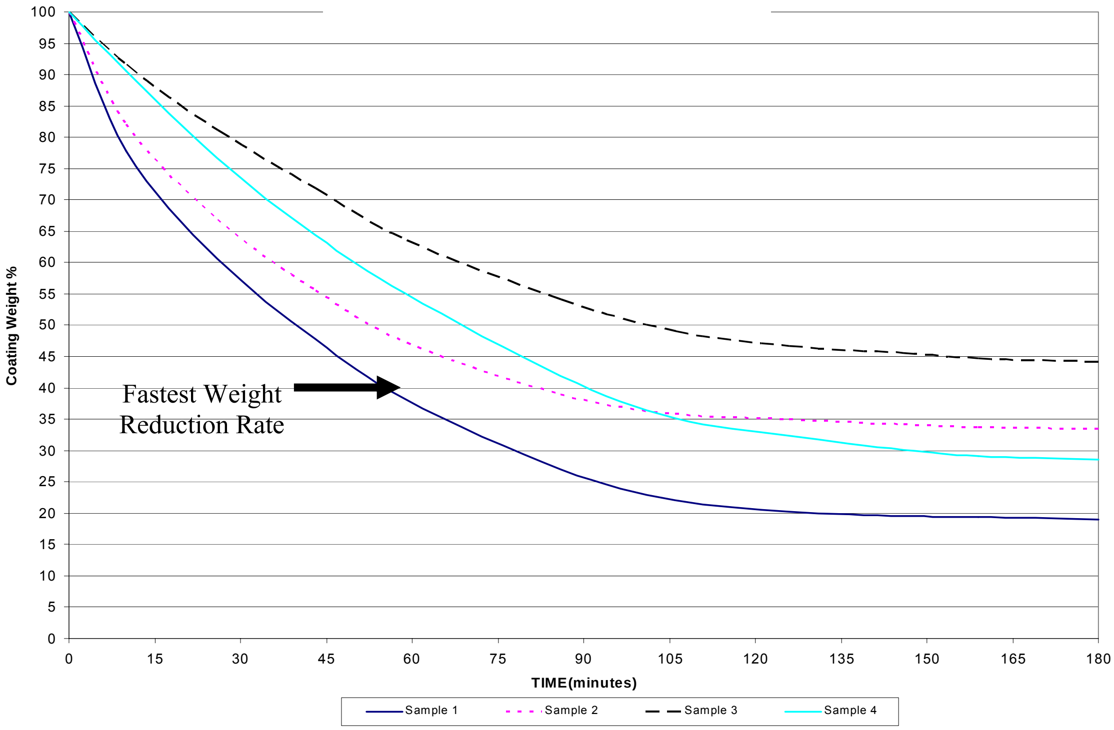

Figure 1.5-3 Data Analysis of Weight Reduction Rate of Formulation Samples.

Figure 1.5-5 shows the different stages of the film curing. Samples 1 and 2 obviously lost solvent at a larger rate while ethanol is evaporated. (RATE 1) As the ethanol becomes less concentrated, water begins to evaporate in a transitional drying period where the rate begins to decrease. (RATE 2) Eventually, all of the ethanol has been removed and the curing rate is limited by the evaporation rate of the remaining free water. (RATE 3) This slope is equivalent to that of samples 3 and 4, which do not contain ethanol. The slowest process step is the removal of water after which all of the “free water” is removed. The remaining water molecules evaporate slower due to interactions between the PVA and water through hydrogen bonding. This accounts for the slow transition from excessively tacky to dry to the touch. (RATE 4)

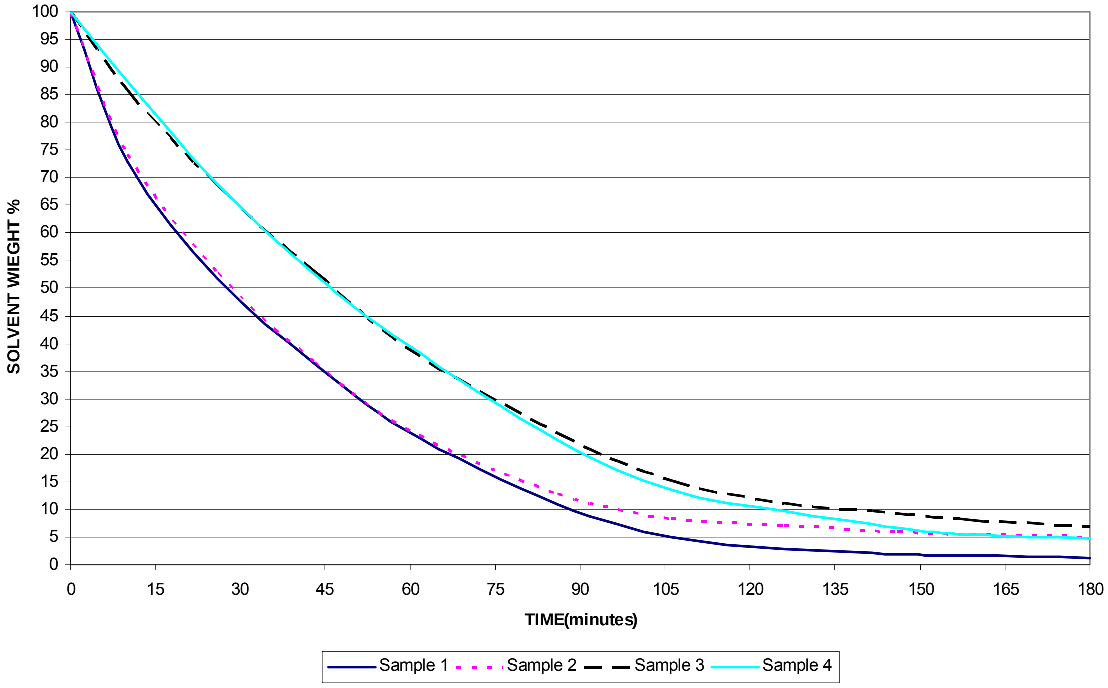

Figure 1.5-4 Data Analysis of Solvent Evaporation of Formulation Samples.

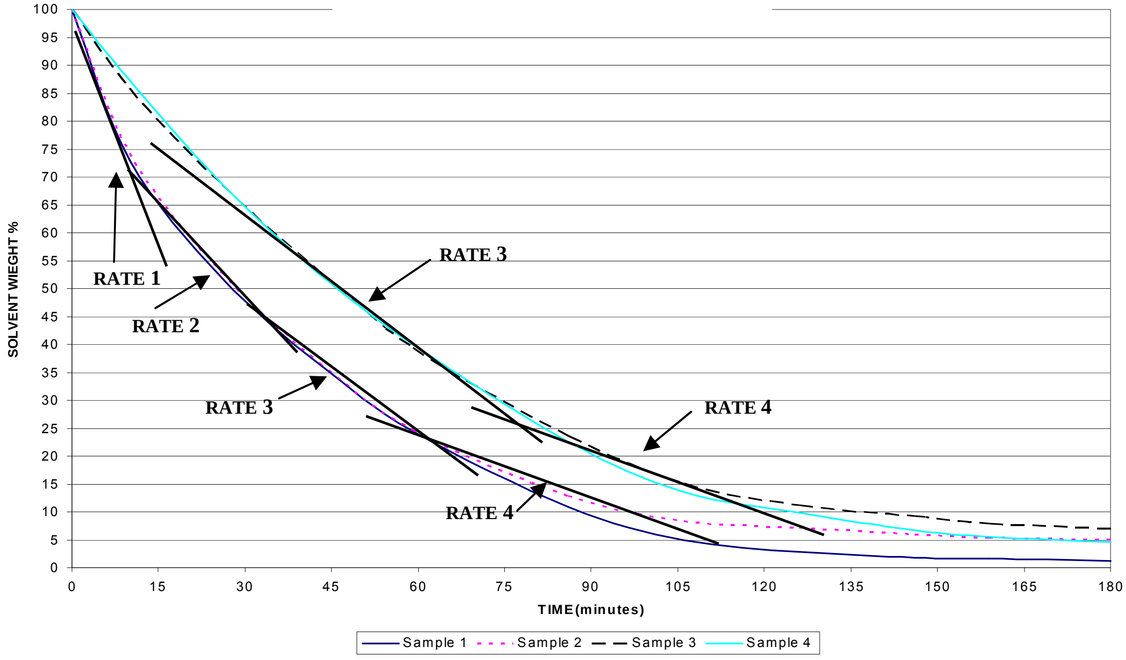

Figure 1.5-5 Multiple Rate of Evaporation Analysis.

1.5.3.2.2 Disadvantages

In order to maintain a liquid at room temperature for long periods of time, a low polymer to solvent ratio is required. (<5 to 1) This means that a lower percentage of the liquid by weight is polymer. This low PVA concentration produces the thinnest of the films and is more prone to running during application. However, the coating tensile strength and tendency to tear is adequate for the project design goals. The standardized methods for determining these quantities are illustrated in the American Standards of Testing Measurements Listing #D 638-01.

1.5.3.2.3 Sample 1 Synopsis.

This sample is an example of the behavior of a room temperature liquid that can be sold in small quantities and does not require heating of any kind. This chemistry produces a less viscous fluid, which produces a thinner coating.

1.5.3.2.4 Future Possibilities.

The PVA concentration can be slightly increased to improve viscosity. Glycerol concentration can also be increased to slightly improve coating elasticity and thickness. The effects of the open cup flash temperature on marketability and transportation cost can be investigated to determine if an increased hazardous shipping classification effects profitability.

1.5.3.2.5 Pigment Coloration.

The coating was given color by adding an orange or yellow pigment. The ability to maintain a constant color shade is important for a number of reasons. By coloring the film either orange or yellow warns plant floor workers of the dangers of handling the coating. Also, by adding colorant aids gives the ability to determine the thickness of the liquid during the application process, which reduces the changes of over or under applying the product. The form by which this color is added is also an important formulation decision. Either a pigment or a dye must be used. Pigments are never solvent soluble by definition. The way that it gives color to the liquid is by dispersing insoluble particles in the solvent solution. These particles will collect in the filters of the oxidation process. In order to avoid this obstacle, a dye must be used. Dyes will give the film an opaque color and allow light to pass through it, making it difficult to determine thickness on a stainless steel wall or floor.

1.5.3.3 Sample 2.

Sample 2 is comprised of a similar formula to Sample 1. The major difference is the increased elastomer concentration. The polymer concentration had to also be increased slightly to account for the increased mechanical separation between the polymer strands caused by the elastomeric additive properties.

1.5.3.3.1 Advantages.

The goal of this coating composition is to exhibit the best possible film behavior. With the entire project goals considered equal, a solution was created that cures quickly and creates a thick, strong coating. Figure 1.5-6 best illustrates the advantage gained in this formula. The time required to reach the point where the film losses its tacky texture is drastically decreased, compared to the other formulas. It is at this point when the overcloth can be applied and the rubber mats installed.

The months of research and testing has produced this formula using two different theories to reduce curing time. By increasing the volatility of the solvent, the evaporation

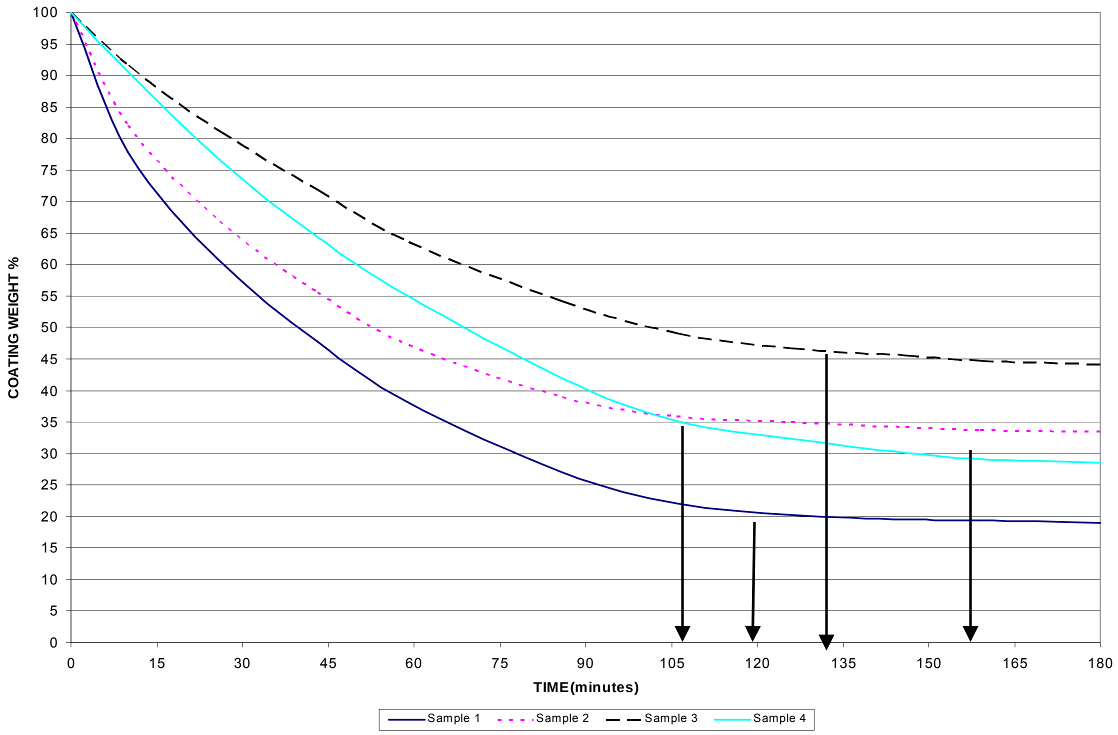

Figure 1.5-6 Analysis of "Dry to Touch" point of the Samples.

rate is increased. The other concept is reducing the physical amount of solvent required in the evaporation process. Higher loading of the plasticizing/elastomeric agent displaces the excess solvent, which allows the dry to touch to occur more quickly. It can be observed from Figure 1.5-7 that the solvent evaporation rate closely mirrors the behavior of Sample 1. The major advantage that Sample 2 contains less solvent to evaporate accounts for the difference in the last 100 minutes of the drying process.

The higher concentration of Glycerol also helps in increasing film thickness and pliability. Of the samples that require reanimation, this sample shows the best response to temperature increases. The high concentrations of glycerol and ethanol reduce the amount of energy required to liquefy the Jello-like state of the shelved coating formula.

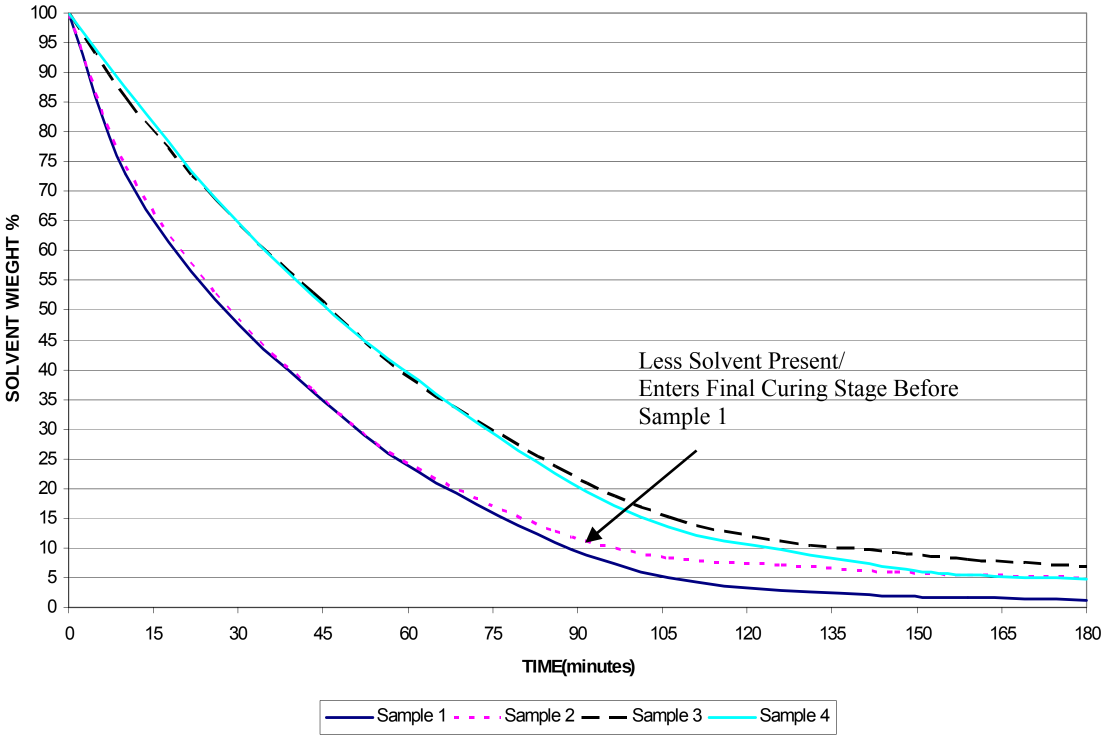

Figure 1.5-7 Final Curing Stage Determination of Samples.

1.5.3.3.2 Disadvantages.

This sample exhibits the best curing times attainable under the design constraints. However, this rapid curing comes with the price of having to be applied with a reanimation process. This forces the use of a heating device 24-48 hours prior to the coating application time. Because of the rapid application, a large volume of the coating must be reanimated in order to assure enough liquid for the proper coating of the refueling pool. This imposes the shipping containers of 55-gallon drums and drum heater as the possible heating apparatus. It is also wise to use heated hoses to insure a smooth uniform coating. This requires a larger investment price, labor instruction and work scheduling by the plant itself. This may be a marketing obstacle unless the time saving attributes are priority one of the power plant's refueling team.

1.5.3.3.3 Synopsis.

As noted above, this formula is representative of the best chemical composition and process of creating a satisfactory coating with the lowest curing time. If the cost of lost time is the main marketability factor. Sample 2 contains the greatest product prospect.

1.5.3.3.4 Future Possibilities.

Further concentration manipulation could result in an even faster curing time. If reanimation procedures are acceptable, higher polymer concentrations will enhance coating strength, thickness and curing.

1.5.3.4 Sample 3.

Sample 3 is comprised of the same polymeric concentration as Sample 2 with an increase in elastomer additive in a solution consisting of only the primary solvent.

1.5.3.4.1 Advantages.

The film produced by this chemical formulation is the best of the testing group. The high polymer concentration produces a strong, thick coating while the high concentration of glycerol keeps the film pliable and elastic. This sample also demonstrates the lowest curing time without the use of ethanol. It accomplishes this by displacing the excess water weight by utilizing a high concentration of glycerol. This allows the sample to reach the dry to touch point faster than the standard stock solution because it retains the highest percent of its original coating weight, illustrated in Figure 1.5-8.

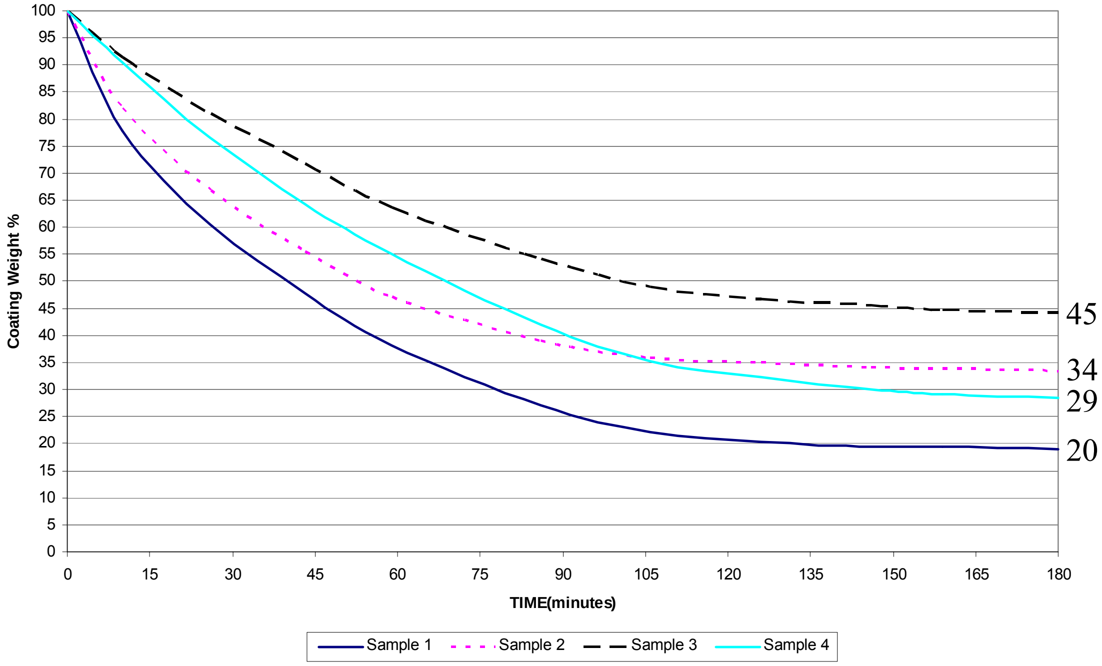

Figure 1.5-8 Analysis of the Final Weight Retention of Sample Films.

1.5.3.4.2 Disadvantages.

This sample produces a slower curing rate than formulas containing ethanol as a partial solvent. The lower volatility limits the evaporation rate, which Figure 1.5-9 illustrates. Due to the similar composition as Sample 2, a reanimation process is required. Another drawback associated with the Sample 3 formula is that the reanimation temperature is increased because of the lack of ethanol. The higher the temperature required to reanimate the liquid relates to longer heating times with the electric drum heaters.

1.5.3.4.3 Synopsis.

If the use of ethanol and highly volatile solvents are prohibited, this sample behavior is the best course of action to decrease the curing time.

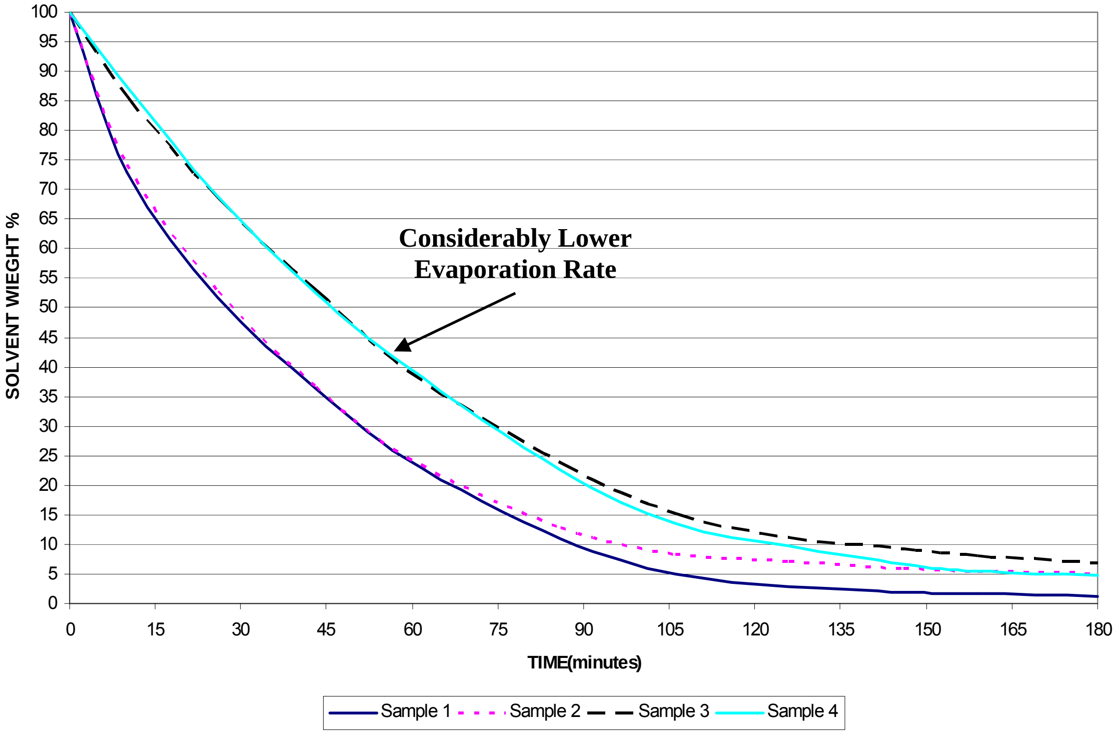

Figure 1.5-9 Evaporation Rate Analysis of the Coating Samples.

1.5.3.4.4 Future Possibilities.

Changes can be made to this formula similar to Sample 2. If reanimation processes are not a major concern, both the polymer and glycerol concentrations can be increased if necessary.

1.5.4 Limiting Design Parameters.

Once the preliminary experimentation data is analyzed, the polymer films inherent properties can be deduced and the inherent abilities can be illustrated. To determine if these behaviors are satisfactory, an investigation into the industrial niche that the product intends to fill must be conducted. This primarily consists of conducting a root cause analysis and discussing the results with seasoned professionals in the field. The major concerns and desired behaviors are outlined below.

1.5.4.1 Drying Time.

One of the greatest concerns to the marketability of the product is the drying time. There is no greater arena in the world where the old adage that “Time is Money” is truer than in the nuclear power industry. A rule of thumb used by outage managers is that \$20,000 in revenue is lost for every one hour that the reactor is not functioning. This means that the drying time of the product formula must be optimized.

The point source of nuclear contaminates presenting themselves as a problem from the refueling processes is not a new phenomenon. Since this source of radionuclieds was identified, the industry has sought after solutions to reduce background radiation levels and contact times in the refueling pool areas. The idea of fixing the contaminates in the matrix of a pealable film is not a novel concept. A film currently available on the market has proven to provide an acceptable decontamination. However, the industry has discontinued its use of the product because of two major flaws. When the film was developed, the average nuclear reactor outage time for refueling and maintenance was approximately 60 days. Current outages are schedule to be slightly under half that time. As mentioned before, time on the plant floor is a valued commodity, which could no longer account for the 8 to 10 hours required of curing time for the product. The impatient nature of the maintenance teams allowed entry into the refueling pools too early in order to gain time or stay on schedule. This premature contact leads to tears in the film, inconsistent decontamination, and improper pealing of the film during removal.

Because of these associated difficulties of working with the films, its use was terminated. The manner in which the area is decontaminated was changed to more time efficient methods.

The current standard of removing the radioactive particles from the stainless steel surfaces of the reactor pool is now conducted by using steam jets to spray the contaminates off the surfaces and onto the floor where washing the area can force the metals into the drains for filtering. The major problems associated with this method are shown in the previous chapter. A fraction of the particles are removed from the surfaces and either remain in the aerosol phase and become an air contaminate or are extracted from the refueling pool and is redeposited to another surface on the plant floor. In either case, the problem is not contained or dealt with, only transplanted to another area of the facility. This problem is currently being assessed by the Energy and Power Research Institute (EPRI). This organization is calling for discontinuing the practice of steam jet use for decontamination in the refueling areas because of the associated side effects.

1.5.4.2 Volatility.

The easiest way to decrease the curing time of the film is to use a more volatile solvent, or a combination of solvents. The associated behavioral improvement associated with the solvent choice is shown in previous sections of this chapter. Unfortunately, the list of chemicals allowed into the refueling pool area or even the plant floor is extremely limited. Because the application surfaces in question are in a recessed area, the accumulation of solvent fumes heavier than air must be considered. Obviously, without proper ventilation, this causes a risk of affixation. Also, if these vapors are flammable, a fire hazard is possible. This is limits the use of solvent to non-flammable, and unfortunately, slower evaporating choices.

1.5.4.3 Waste Reduction.

Another reason for developing new technology in place of the current pealable coatings is the removal costs. Any material that leaves the reactor building must be tested for radioactivity. Because the coating is embedded with radioactive particles, the radioactivity of the film is much higher than allowable for regulation refuse. Because the current market decontamination film is latex based, the plant is forced to pay the costs of either burying or incinerating the contaminated film. In either case, the cost is based not on weight or contamination level, but by volume. The pealable film, particularly rolled, consumes an extremely large volume. The removal costs must be addressed and optimized in order to satisfy the profitability of the desired market.

1.5.4.4 Application Techniques/ Application Time.

Another constraint that must be considered in the development of the product formula is the technique and associated time involved in initially applying the polymer coating. This process must be relatively simple and time effective. It is best, from a marketability aspect to use equipment that can already be found on the plant floor or equipment that is industry accepted. Any use of custom made equipment or new designs are difficult to implement in situations where time and dependability are priority one. An airless sprayer is used on the plant floor for painting purposes. Former latex decontamination films were also applied using similar piston pump style airless sprayers.

It is important to understand the mechanics of this equipment in order to determine it's capabilities and limitations.

1.5.4.5 Airless Sprayers.

An airless sprayer is comprised of an electric motor and a piston pump. The motor is the power source and revolves at a rate (RPM) that must be reduced before the power is transferred to the piston rod. This is accomplished through internal gear reductions. Once the speed is reduced, the motors circular motion is converted to linear motion by using the eccentric bearing and scotch yoke. The scotch yoke is connected to the piston rod forcing it up and down. This up and down motion forces the fluid into the filter housing and hoses leading to the sprayer gun where the coating is put under pressure. Once under pressure, the coating is forced through a small opening (the tip) and broken into small droplets (atomized) making the coating spray able. This process is illustrated in Figure 1.5-10.

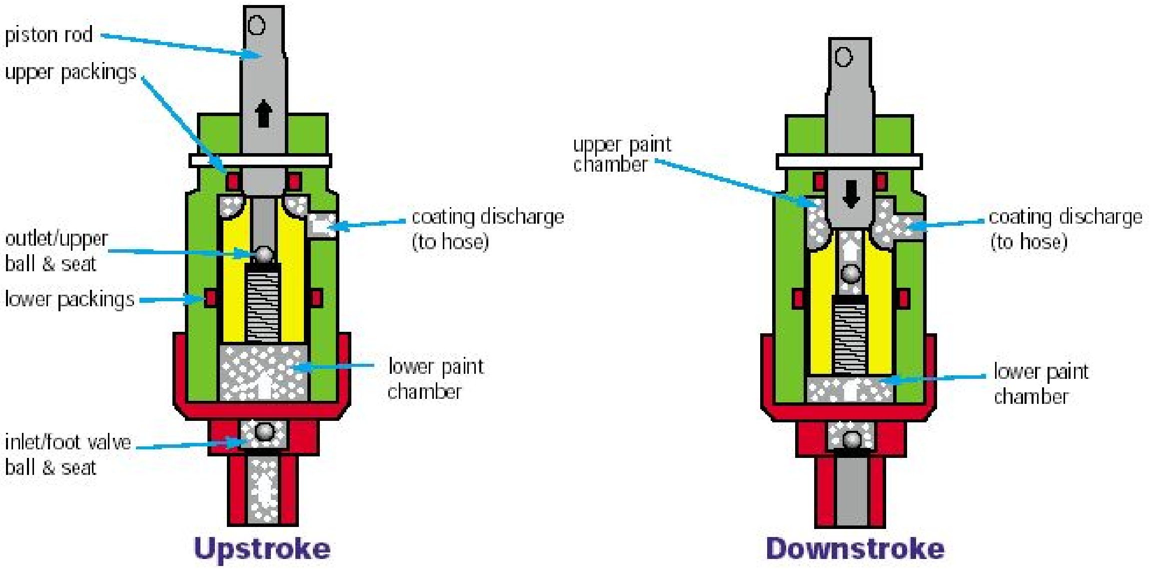

Figure 1.5-10—Piston Pump Mechanical Diagram.

On the upstroke of the piston, the paint in the upper paint chamber is compressed (pressurized). After the coating is under pressure it is discharged through the hose to the gun and forced through the tip. The upper ball is forced against the upper seat, creating a vacuum and pulling the inlet ball off the inlet seat, which allows paint into the lower paint chamber. As the piston moves down, the inlet ball is forced against the inlet seat and the outlet ball is lifted off the outlet seat. Coating in the lower paint chamber is forced through the piston rod into the upper paint chamber. Because the upper paint chamber is only half the size of the lower paint chamber pressurized paint is again discharged through the hose, gun and a tip. This is known as a dual acting piston that allows pumping paint on both the upstroke and down stroke.

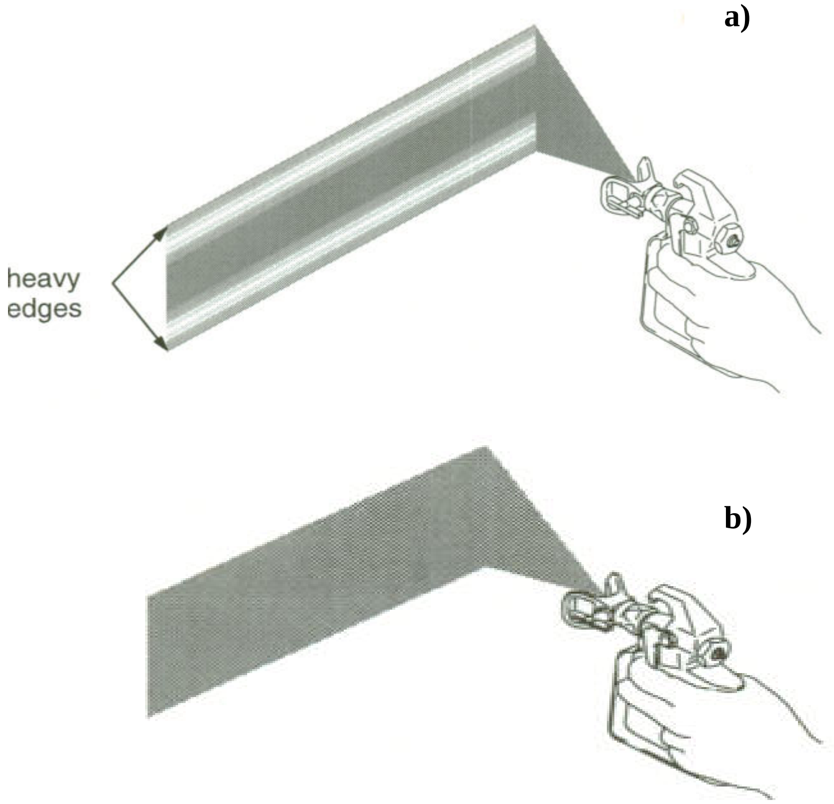

Figure 1.5-11 Spray Pattern Determination.
a) High Viscosity Coating
b) Proper Uniform Spray Pattern

In order for a uniform atomization of coating droplets to occur, enough pressure must be present to overcome the viscous and surface tensions forces at the tip of the prayer gun. Figure 1.5-11 illustrates the effects of an overly viscous fluid at a predetermined set pressure. If the pressure required to properly spray the material surpasses the maximum pressure of the apparatus, a less viscous formula must be developed.

In order to test this limitation, the Graco Ultra 395 dual acting piston airless sprayer shown in Figure 1.5-14 was used to test the capabilities of this type of machinery. This particular equipment can serve to apply the polymer coating in one of two configurations. The most commonly used approach is to use an airless sprayer attachment that produces a uniform fan spray of liquid. This approach limits the viscosity of the fluid that can produce this even spray. The required equipment includes the items shown in Figure 1.5-12.

In order to utilize formulas with higher viscosities, a roller attachment system can be employed. This consists of a specialized handle that allows greater flow rates to a telescopic extension that leads to a roller knap fluid distributor. An example of this system in shown in Figure 1.5-13. The roller knaps used in this system can be easily made from polyvinyl alcohol polymer fibers, which allow the only piece of equipment to come in contact with the contaminated surface to also be processed with the film. This is consistent with the project goals and maintains the aim of solid waste reduction. The differences in application technique relates to changes in coating thickness, film durability, curing time, application time, and this form of application produces a thicker, more durable film coating.

Figure 1.5-12 Paint Sprayer Gun with Multiple Size Orifice Tips.

Figure 1.5-13 Paint Roller Attachment Set.

Figure 1.5-14 Test Equipment (Graco Ultra 395 Dual Action Piston Pump Paint Sprayer).

Also, it is best to use the fewest pieces of equipment required to produce an adequate coating. At high concentrations of polymer content, the liquid thickens to an unpumpable state. In order to break this solid lattice, the material must be reanimated in a specially designed processor to reduce the viscosity back into the region in which pumping can occur. Although this extra step doesn't relate to longer application times, it does however, require more management scheduling to assure that the coating can be applied at the moment that the technicians responsible for decontaminating the refueling pool are allowed access. A special testing area was developed to mimic the behavior of the surfaces in the refueling pool area. Two vertical walls were constructed at a 90 degree angle to form a corner. This is an important because maintaining a uniform coating at the intersection of the two walls is critical. A floor section to study the horizontal behaviors of the polymer coating connects these walls. A schematic of this testing device in shown in Figure 1.5-15.

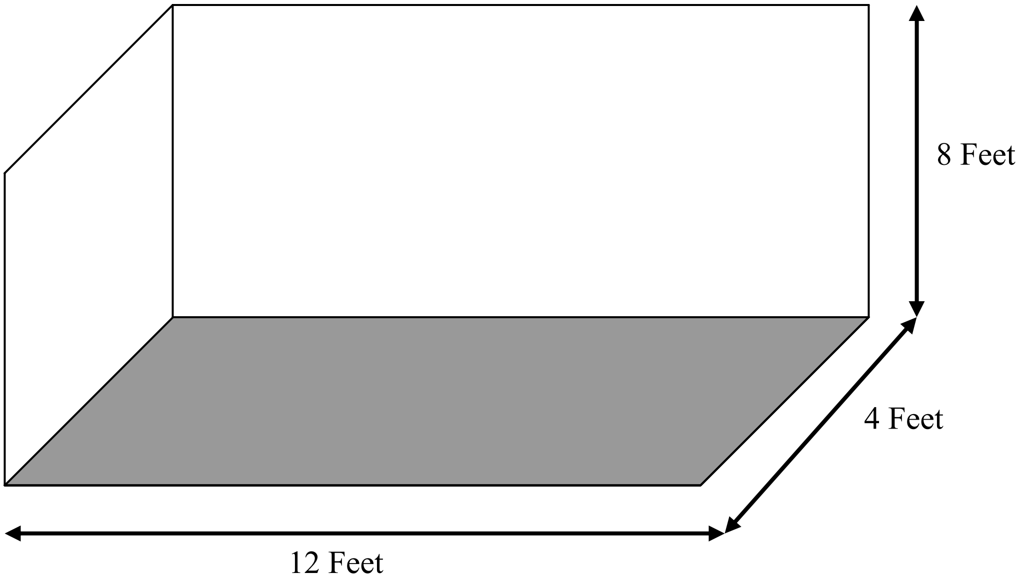

Figure 1.5-15 Metallic Testing Wall Surfaces Diagram.

1.5.4.6 Coating Film Thickness.

The thickness of the film is not a primary optimization parameter. The major behaviors of the film that must be exhibited are the tensile and tear strength of the film during the removal stages from the contaminated surfaces. These behaviors were tested by experiments that were adapted for this particular application. The original laboratory experiments are given in the standards provided by the American Society of Testing and Measurements #D 638-01 & #D 5735-95.

The time required to remove the film is just as important as the application time. If the coating does not maintain uniform integrity, the removal time increases dramatically. This is especially true in the confined area around the refueling pool such as drainage ports, piping gaskets and the reactor head manifold. Another important aspect of the coating thickness is the coloration choice. In order for proper application, the film must contain enough colorant to be able to illustrate a contrast to the color of the stainless steel surfaces. Even though the formula is designed to produce a given thickness, without proper installation, the behaviors will not be shown. Examples of this color optimization obstacle during application is illustrated in Figure 1.5-16 & Figure 1.5-17.

Figure 1.5-16 Unacceptable Coating Color Concentration.

Figure 1.5-17 Acceptable Coating Coloring Concentration.

1.5.4.7 Viscosity.

The viscosity of the coating fluid is one of the primary design constraints of the system. This intrinsic property has influences on many of the optimized coating behaviors including application technique, tensile and tear strength, film thickness, and redissolvablility. All testing of viscosity was conducted using a Brookfield Viscometer apparatus and the standardized methods and procedures are outlined in Appendix D. One important fact needed for this parameter to be optimized is an accurate model to predict the viscosity of a given formula.

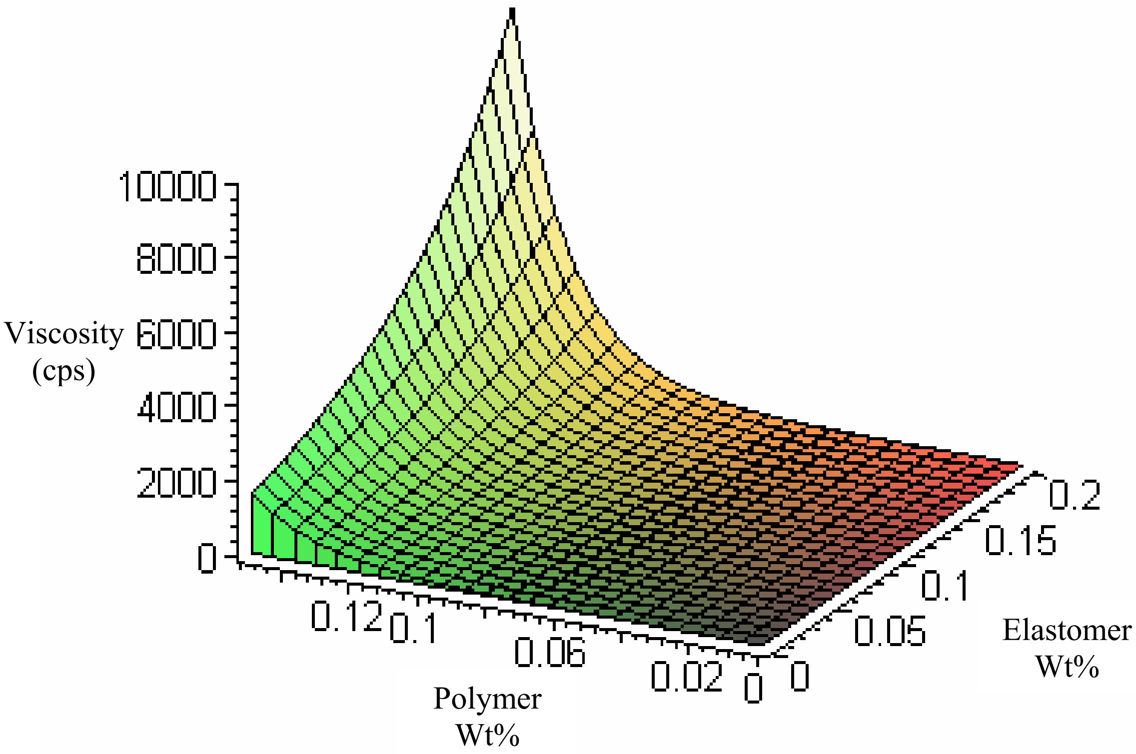

Figure 1.5-18 Viscosity Surface Analytical Model.

By conducting multiple experiments with varying formulas, a set of mixing rules for the systems were developed. This can be best implemented by graphing this empirical model over the two major component concentrations, polymer and elastomer. The resulting surface is illustrated in Figure 1.5-18, where any one point relates to a formula mixture.

By performing an overall coating system optimization, an optimal viscosity range can be determined for different application techniques. Once this is established, a surface plane is introduced at the design viscosity and creates a cross section of the viscosity surface. This cross section results in a function that links polymer concentration to elastomer concentration. By developing the constant viscosity behavior curve, the ratios of the proper amount of solvent and additives to be incorporated for different polymer grades and blends can be determined. This process is shown in Figure 1.5-19.

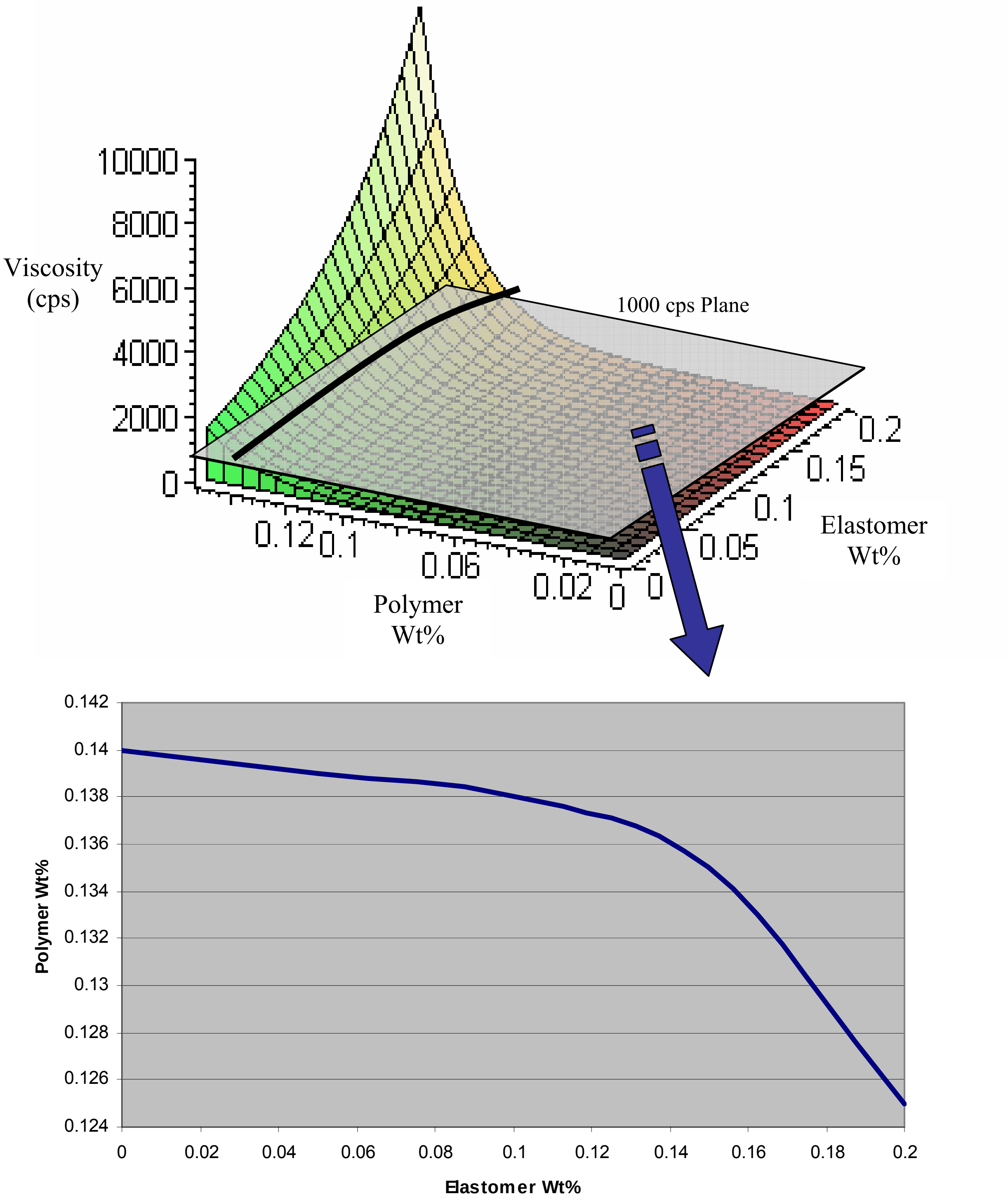

Figure 1.5-19 Formulation of Determining the Constant Viscosity Model Process.

1.5.4.8 Decontamination Factor.

The most important design parameter that the product must exhibit is a quantitative behavior known in the industry as the decontamination factor. The ability of the film to remove contaminates from surfaces is measured by the ratio of radiation detected before the coating application to the radiation after the product film removal. The manner in which the radiation is measure is dependent on the types of equipment available. For example, Gamma Spectroscopy allows for exact measurements of particular contaminant presence before and after the testing by using a smear test approach.

The decontamination factor is a major marketing parameter that must be experimentally proven to be equivalent or exceed current industry established market products or procedures. This style of testing was not only used to determine industry standards, but also to determine the major driving forces in the mass transfer of the film. By varying the concentration of additives to the formula, it was determined that the addition of metallic absorbing chemicals did not affect the decontamination factor of the material. This shows that the major driving force of the system to retain the metal contaminants is the mechanical entrapment parameters surrounding the polymer matrix of the film. Examples of this data are shown in Table 1.5-1.

Table 1.5-1 Gamma Spectroscopy Determination of Coating's Effective Decontamination Factors.

Coating Formula	Activity Prior (DPM)	Co-60 Prior (uc/ea)	PostStrip Activity (DPM)	PostStrip Co-60 (uc/ea)	Decon. Factor
TLCStripCoat	12,000	1.61E-02	1,000	1.13E-03	14.3
Orex Decon. I	8,000	1.45E-02	<1,000	6.58E-04	22
OrexDecon II	35,000	4.61E-02	<1,000	2.84E-04	162.5

It can be shown from this data that the Orex blend of polymeric decontamination film can generate larger decontamination factors than its competitors. In order to defend this statement, the measurements were observed in two different manners. Radioactivity is reported in "DPM" or disintegrations per minute. One "curie" of activity is equal to 3.7E10 disintegrations per second. So "uCi" is the abbreviation for micro-Curie or 1E-06 Curies. Samples with initial starting activities prior to the film applications higher and lower than the competitor's product are reported to show that the initial level of activity did not influence the post stripping activity values. In both cases, the Orex formula was able to attain lower remaining activity levels because more of the metal contaminates were removed by a tighter laced polymer matrix. In order to prove this attribute, Gamma Spectroscopy was conducted to trace particular metal particles. By using the surface swab techniques outlined by the American Society of Testing and Measurement standards, a testing area was wiped with a testing swatch. This swatch, once analyzed, gives a relative concentration of metallic particles by conducting the gamma spectroscopy measurements. Table 1.5-1 shows that the Orex polymer films consistently removes an order of magnitude more material from the surface by monitoring the most prevalent contaminate, Cobalt 60. These lower uncaptured values are attained even when larger amounts of Cobalt 60 are present on the pre coating surface. It is important to utilize these behaviors in the optimization of the formulation to develop a product that is extremely effective, marketable, and profitable.

1.5.4.9 Redissolvability and Disposal Processes.

The processes of dissolving polyvinyl alcohol into water and degrading to polymer through an oxidative processor are currently used on a daily basis by the Orex Technologies, Incorporated organization. It is imperative that the decontamination film breaks down in this already functioning process. There are many different film attributes that relate to the behavior of the coating during this disposal process. If the coating is too thick, a larger residence time in the processor is required to fully dissolve and oxidize the coating. The initial polymer concentration increases the cured film density and also requires longer reaction times. Another consideration is the behaviors of any additive, pigment, or blended polymer other than polyvinyl alcohol. Any ingredient must able to conform to the design of this redissolvability and disposal process. This portion of the decontamination system is vital to include in the overall product optimization because it allows minimizing the amount of effluent from the process. By including the formula behavior to disposal process, the “cradle to grave” formula optimization approach can be successfully utilized.

1.6 Proof of Concept Conclusions and Data Analysis.

By analyzing the individual behaviors of polyvinyl alcohol polymer films, it has been shown that a viable solution to the nuclear power plant refueling pool decontamination crisis is feasible. The opportunity to develop a successful, marketable, and profitable product is reasonable. However, to access the full benefits of the product system as a whole, advanced modeling and optimization techniques must be employed to predict the severe non-linearities in the product performance. Using a trial and error approach to this formulation optimization would be very time consuming and pricey.

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CHAPTER 2 A SYSTEMATIC APPROACH FOR SYNTHESIS OF OPTIMAL PRODUCT FORMULATIONS:

A CASE STUDY IN POLYMER FILMS FOR RADIOACTIVE DECONTAMINATION AND WASTE REDUCTION.

In this work, an effective and systematic modeling technique is devised to generate optimal formulations for explicit material product engineering applications. These methods aim at developing quantitative values for not only intrinsic properties, but qualitative characteristics are developed in order to simultaneously optimize the formulation subject to the product specifications. The predictive modeling framework developed is comprised of material and energy balances, constraint parameters, constitutive equations, design/optimization variables and possible synthesis techniques. This contribution illustrates a novel means by which a large range of material behavior based compounds and mixtures can be evaluated with fewer testing iterations. These modeling techniques are illustrated in a case study creating a new polymeric surface decontamination product for nuclear power production applications. In this example, a set of user defined design constraints produces a subset of different optimization formulations comprised of different polymer blends, molecular weights, hydrolyzation extents, solvents, and additives.

In the pages to follow, it will be shown that this project, published in the Journal of Computer-Aided Chemical Engineering--Volume 20B, is a successful example of the evaluation of:

1) Formulation Synthesis.
2) Integrated Product Design.
3) Material Development.
4) Reverse Property Prediction.

2.1 Introduction.

Formulation of new products and improvement of existing merchandise is practiced in many different industries including paints and dyes, polymers and plastics, foods, personal care, detergents, pharmaceuticals and specialty chemical development. Current trends in the engineering design community have moved towards the development of quantitative integrated solution strategies for simultaneous consideration of multiple product characteristics. The optimization variables are most often determined by qualitative attributes, stochastic variables, visual observations and/or design experience. The effectiveness of these approaches is limited by available data, bias towards specific solutions, reproducibility, and experimental error. Model insight is required for development of fast, reliable and systematic screening methods capable of identifying optimal formulations and reducing the number of subsequent laboratory trials.

2.2 Model Development Methodology.

In order for the product to exhibit the desired performance, a combination of discrete constraints must be fulfilled. Identification of an optimal formulation that is suitable for the desired system requires integration of all the interlacing behaviors of the product constituents. These characteristics include the constituents used for construction as well as their inherent properties. This is accomplished by using a combination of novel modeling techniques.

2.2.1 “Cradle to Grave” Optimization

In the hazardous material management and governmental regulation compliance fields, there is a concept known as “cradle to grave” liability for hazardous materials producers. The Resource Conservation and Recovery Act (RCRA) of 1976, which amended the Solid Waste Disposal Act, was the first substantial effort by the United States Congress to establish a regulatory structure for the management of solid and hazardous wastes. This set of regulations yielded a complex assortment of regulations governing the management of hazardous waste from the cradle to the grave. Specifically, Subtitle C of RCRA addresses this "cradle-to-grave" concept and the associated requirements for hazardous waste from the point of generation to disposal. Even though product formulation rarely has anything to do with hazardous material develop, our optimization technique adopts a similar concept, maximizing all the product behaviors between development and disposal.

Typical product development and the associated processing systems in industry occur in three separate stages; formula creation, production design and waste management. Not only do different groups of chemists, engineers and scientists generally conduct these three stages of construction, but also different companies and institutions. New products are formulated in laboratory experiments to improve on existing industrial niches or to create completely new markets. These formulas are optimized to produce the best possible product behavior in order maximize marketability and profitability. This product recipe is then passed on to the process development researchers to determine the optimized manufacturing system of equipment, chemistry and fabrication methods. It is not uncommon to outsource production to entirely different companies, with can separate the goals of product creation and process equipment usage. Even though this network of equipment is also optimized with consideration to production rate, manufacture efficiency and profitability, the optimized product train is limited to processes that only produce the independently optimized product formula. The combination of the product formulation and manufacturing process creates an entirely new system that must be optimized. Even though the formula and process are considered optimal, because they were determined independently from one another, the overall system may not be at the peak of working conditions. Because of non-linearities in chemistry, thermodynamics and mechanics, small changes in product formula may relate to drastic changes in the production requirements and vise versa. In the case of products that are not completely consumed or create byproducts, the waste and refuse processes creates another process associated with the formula. A separate company or institution generally conducts this process, whether it is water treatment, recycling, destruction, or land filling. As in the production process, small changes in the formula can create drastic changes in the waste management aspects of the product. These independent process optimizations are illustrated in Figure 2.2-1.

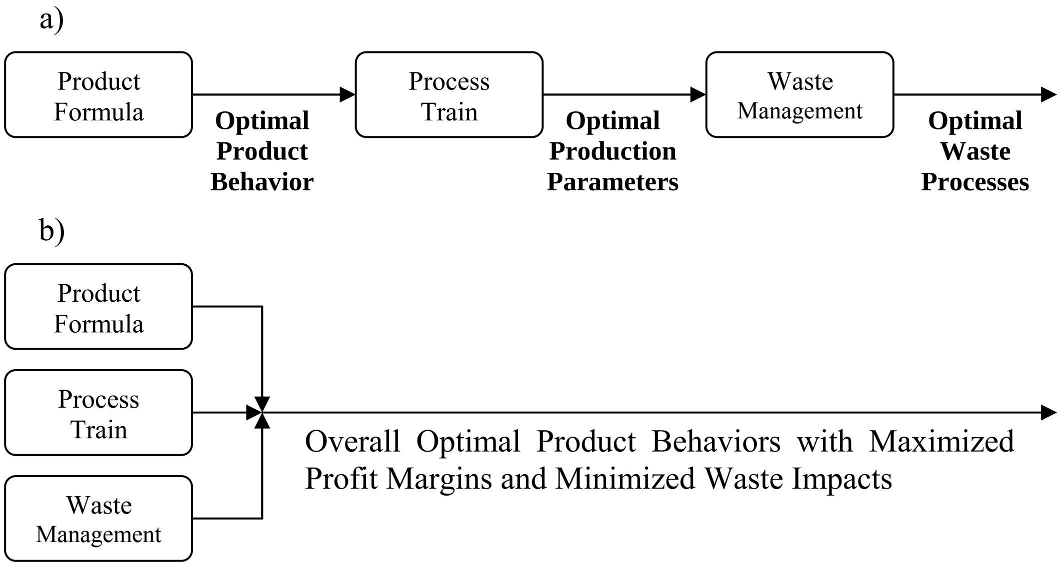
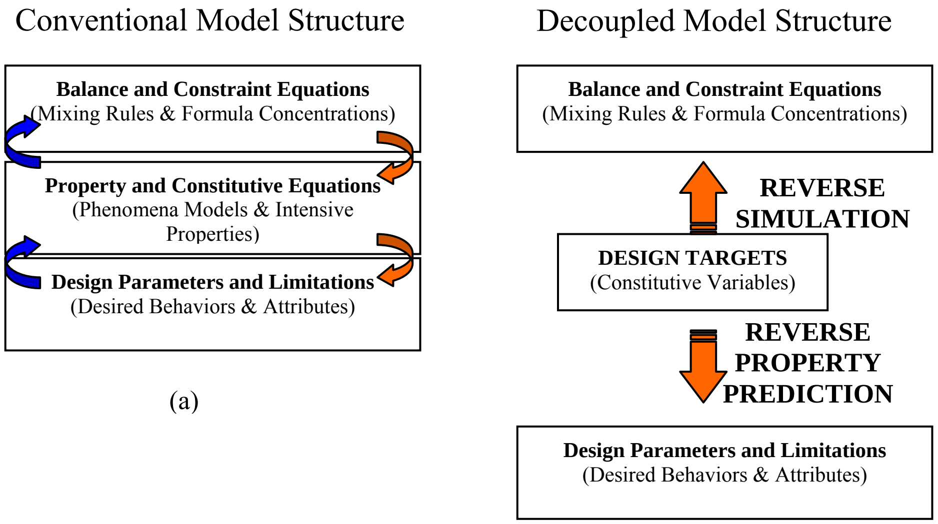


Figure 2.2-1 Process Optimization Techniques.
a) General Formula Development and Manufacturing Process Optimization Practice
b) Cradle to Grave Product Optimization

With the increasing pressure of reducing contaminate regulations of wastewater streams, new techniques of maintaining governmental compliance must be developed. By applying the concept of “cradle to grave” responsibility to product formulation, a reduction in measured effluent parameters can be achieved. This is accomplished by optimizing the product formulation and production process to reduce the amount of associated byproduct that must be disposed of. By optimizing the product formula, process parameters, and disposal procedures simultaneously, shown in Figure 1(b), the entire system produces acceptable product behaviors, maximum manufacturing process profitability and efficiency, and minimum waste impacts and costs. In order to access the full benefits of this product system optimization, novel modeling techniques must be employed to predict the severe non-linearities in the product performance throughout it's life cycle.

2.2.2 Property Integration

The first step in developing this "cradle to grave" model is property integration. This method consists of tracking functionality instead of chemical species in order to represent the synthesis problem from a property perspective. The conventional approach to product formulation development is selecting constituents that exhibit desired produced properties and optimizing the mixing ratios. In order to model the product characteristics, these pre-determined candidate components are required as inputs to the design algorithm. These input choices are based on qualitative process knowledge and/or design experience, which can exclude solutions involving other possible raw material sources. In this work, the concept of property integration for process development introduced by El-Halwagi et al. (2004) is applied to product synthesis. This modeling approach allows for solution of many different engineering problems to be conducted on a property only basis. This method allows for identifying optimized solutions to specified chemical engineering problems by determining the desired output and solving backwards for the constituents and compositions. In the case study to be described in the next section, these techniques are used in conjunction with a model decomposition technique to allow for formulation of reverse property prediction problems. By employing this technique along with a model decomposition technique, the complexity of solving for both non-linear solutions to composition and behavior is separated into two separate, less complex models.



(a)

(b)

Figure 2.2-2 Decoupling of Constitutive Equations for Reverse Problem Formulation.

2.2.3 Model Decomposition/Reverse Property Prediction.

These modeling techniques are useful tools to reduce the complexity involved when trying to simultaneously optimize balance and constraint equations with constitutive and property models. The in depth processes involved with applying these novel techniques has been described by Eden et al (2004). Although this procedure was created for process development, minor changes allow for application to product design. The main objective of this process is to separate the balance and constraint equations from the often complex and non-linear constitutive property relations. Figure 2.2-2 illustrates this decomposition principle by showing how the overall model (a) is divided into two separate models by defining target property variables (b). These target variables are a set of solutions to both the formula balance model and the constitutive property design model. Each mathematical system is solved independent of the other until valid sets of solutions are found that satisfies both networks. This technique is illustrated in the following case study.

2.3 Case Study – Polymer Film for Nuclear Applications.

The desire to decontaminate surfaces inside nuclear power plants has been addressed with a number of different products. The implementation of latex-based pealable films has been used for many years. The coating serves to initially “fix” the contaminants in place for containment and ultimate removal. However, power plants have discontinued the use of these products because of their long drying times and expensive disposal costs. In the place of these products, protocol has turned to the use of steam jets to remove the radioactive particles and clean the exposed surface. This method has proven to be ineffective due to a build up of contaminants that, through molecular transport, become airborne and contaminate larger areas. The purpose of this work is to develop an effective and systematic model to synthesize a formulation of a water soluble polymer film coating for radioactive decontamination and waste reduction. This material development involves the use of a polymer matrix that is applied to surfaces as part of the decontamination system in place of the past latex products. Upon mechanical entrapment and removal, the polymer coating containing the radioactive isotopes can be dissolved in a solvent processor, where separation of the radioactive metallic particles occurs. Ultimately, only the collection of filtered solids must be disposed of as nuclear waste. The ability to identify such a product creates an attractive alternative to direct land filling or incineration. In order for the polymeric film to be a viable candidate, it must exhibit the desired performance that previous coatings are unable to. These characteristics include, drying time, storage constraints, decontamination ability, removal behavior, application technique, coating strength and dissolvability processes.

2.3.1 Property Integration of Polymer Coating Model

Identification of an optimized formulation that is suitable for this entire decontamination system requires integration of all the interlacing characteristics of the coating composition that affect the film behavior. In order to accomplish this, an accurate representation of the system must be developed in order to solve the design parameters in terms of properties only. The representation of the design parameters along with the interactions between them and the overall formula behavior is given in Figure 3. This model could be solved as a reverse simulation using the final coating characteristics as input variables and the final polymer, solvent, and additive selections established as output solutions. The intricacy here is producing an accurate model, as the inherent non-linearity of the property relationships in conjunction with the complex formulation balance equations makes acquiring viable solutions difficult. In order to overcome these obstacles, the process of model decomposition is employed.

2.3.2 Decomposition of Polymer Film Design Problem.

Before the optimization system can be decomposed into separate parts in order to reduce the complexity of simultaneously determining an optimal process solution. These subparts are comprised of formula equations, design parameters, and target property values. However, this process of determining and tracking functionality instead of chemical species had to be modified from the technique presented by Eden et. al. (2004). Consideration for the multiple desired properties for a material product behavior causes a different separation in the model decomposition structure of the system than in the technique's industrial process equipment counterpart. An extra step of defining observational design behaviors into measurable properties is required. This subtle modification is illustrated in Figure 2.3-1.

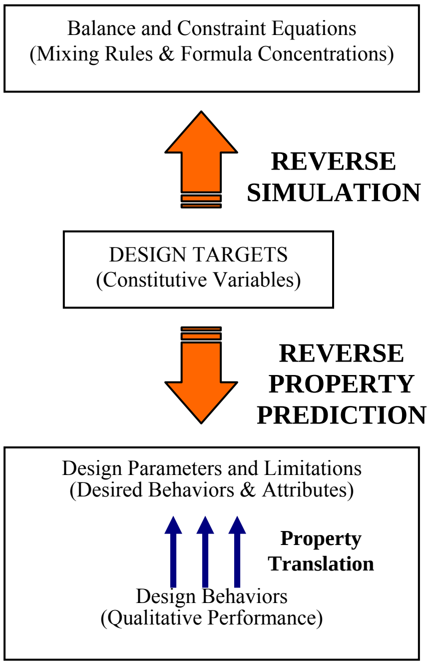


Figure 2.3-1 Decoupling of Case Study Model for Reverse Simulation.

In this specific project example, the design parameters and limitations are comprised of properties in two separate classes. Class I Properties consist of physical properties that are related to the formula constraints such as composition, temperature, density, and viscosity. These properties are the values tracked under normal system conditions for which this technique was originally designed. But, because this particular system is driven by application behaviors which are not directly chemical controlled, another classification of properties arise, which are not directly related to an intrinsic property. These attributes, referred to as Class II Properties includes specific performance oriented variables such as decontamination ability, application technique, removal processes and disposal methods. These Class II Properties must go through a translation step form qualitative and quantitative performance observations into numerical physical property values. Once this additional step is included in the definition of the design parameters, the entire decomposition step can commence, which is illustrated in Figure 2.3-2.

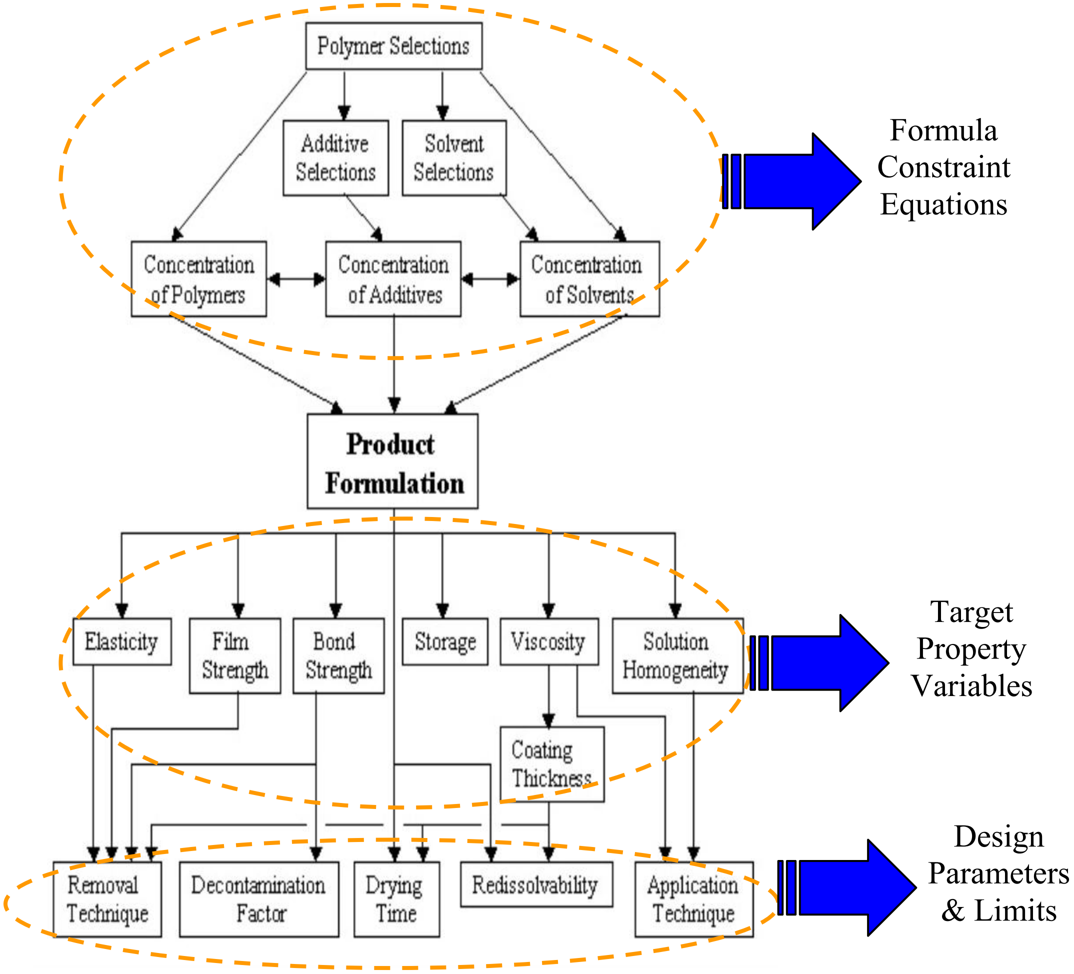


Figure 2.3-2. Schematic Representation for Polymer Film Design & Model Decomposition.

2.3.2.1. Formula Constraint Equations.

The formula balance equations are separated into a reverse simulation that includes polymer, additive and solvent choices. Among these selections are available synthesis variables that affect polymeric properties such as molecular weight and extent of hydrolysis. With this information included in the model, not only can different polymer chains be compared, but also different variations of the same polymer and polymer blends. The ability to optimize the polymer synthesis as well as the film composition increases the possible formula combinations and improves the chances of acquiring an acceptable optimized formula. The additive options include components that enhance the desired film properties in order to fulfill the necessary constraints from the target property variables. This assortment of compounds contains wetting agents, surface tension reducers, biocides, cross-linking agents, elastomers, resin hardeners, dyes, pigments and dispersants. The choice of solvents is limited not only by the polymer selection, but also by the application. The list and amounts of volatile solvents allowed to be used on a nuclear power plant floor is extremely limited. The initial concentration of solvent present in the coating is the primary driving force involved with drying time. It is imperative for this part of the overall model to simultaneously optimize the formulation so that target properties are exhibited and the overall film behavior is superior to current competitor products.

2.3.2.2. Design Parameters.

The design parameters and limitations represent a compilation of attributes that the final product must exhibit. Because this formulation is intended to fulfill a market niche that already exists, the final formula characteristics are well known. The primary design parameters are the decontamination ability, drying time and redissolvability. The ability for the film to remove contaminates is measured by the ratio of radiation detected divided by the radiation present before the film removal. This numeric value is known as the decontamination factor and is a major selling point that must be equivalent or better than other possible decontamination products and processes. Another parameter where the new formulation must out perform the competing processes is drying time. Nuclear power plant outages are very costly and the schedule is optimized to minimize profit losses. By producing an optimized formula with the customer's major objectives in mind increases the marketability of the product and improves possible sales. The issue of redissolvability mostly pertains to the manner in which the film is disposed of. The current operations in nuclear plants involve the use of many different polymer based products that are sent to processing stations for redissolving and filtering. It is desired that the film can be disposed of by utilizing these same processing procedures. Other constraints include a simple and effective means to apply the coating to the walls and surfaces inside the plant as well as removal techniques. The model's main objective is to determine what intrinsic properties govern the desired performance variables and develop a dynamic set of target properties.

2.3.2.3. Target Property Variables.

The development of a set of target properties allows this model to utilize reverse property prediction to identify the design alternatives. This is accomplished thru experimentation to determine what property ranges equate to final film behavior. In order to illustrate the modeling techniques presented in section 2, we can simplify the system by assuming that the only major target property in figure 2 is viscosity, which is the primary design constraints of the system because it's influences on many of the optimized coating behaviors including application technique, tensile and tear strength, film thickness, and redissolvablility. This simplified model is decoupled into two separate systems, the chemical makeup equations that produce a given viscosity and the behavioral models, which predict how the viscosity affects the design parameters and limitations.

The analysis of experimental data from formula variation tests produces a set of mixing rules for the system. When graphing this empirical model on over the two major component concentrations, polymer and elastomer, the resulting surface is illustrated in Figure 2.3-3, where any one point relates to a formula mixture.

By conducting laboratory tests and models to quantify the qualitative design behaviors, the optimum fluid viscosity that produces an adequate application behavior can be determined to be a given value, 1200 centipoise for example. This value becomes the viscosity design target of the qualitative prediction model. Once this is established, a surface plane is introduced at the design viscosity and creates a cross section of the viscosity surface. This cross section results in a constant property function chart that links polymer concentration to elastomer concentration. By developing this constant viscosity behavior curve, the ratios of the proper amount of solvent and additives to be incorporated for different polymer grades and blends to produce the desired property. This process is shown in Figure 2.3-4. These techniques seem unnecessary when considering only one target property, but when numerous targets are set, these simplification processes are extremely advantageous.

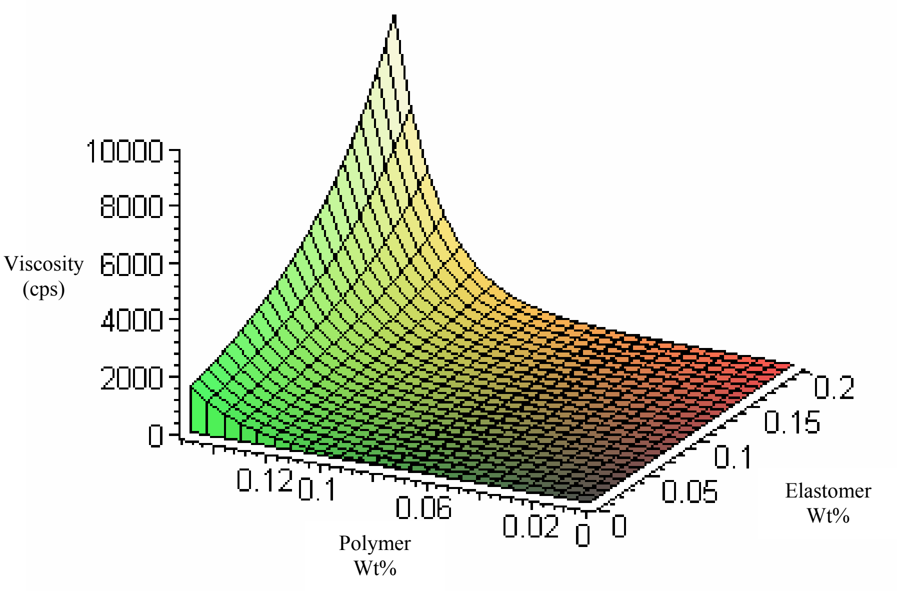


Figure 2.3-3. Viscosity Three Dimensional Analytical Model.

2.4 Results from the Optimization Techniques.

The ultimate result of this model aided in the development of a product that increases the removal rate of radioactive contaminates by 69% while attaining a 33% reduction in drying time over the current marketed competitors. The finalized product formula will be available through the Orex Technologies Catalog in Fall of 2005.

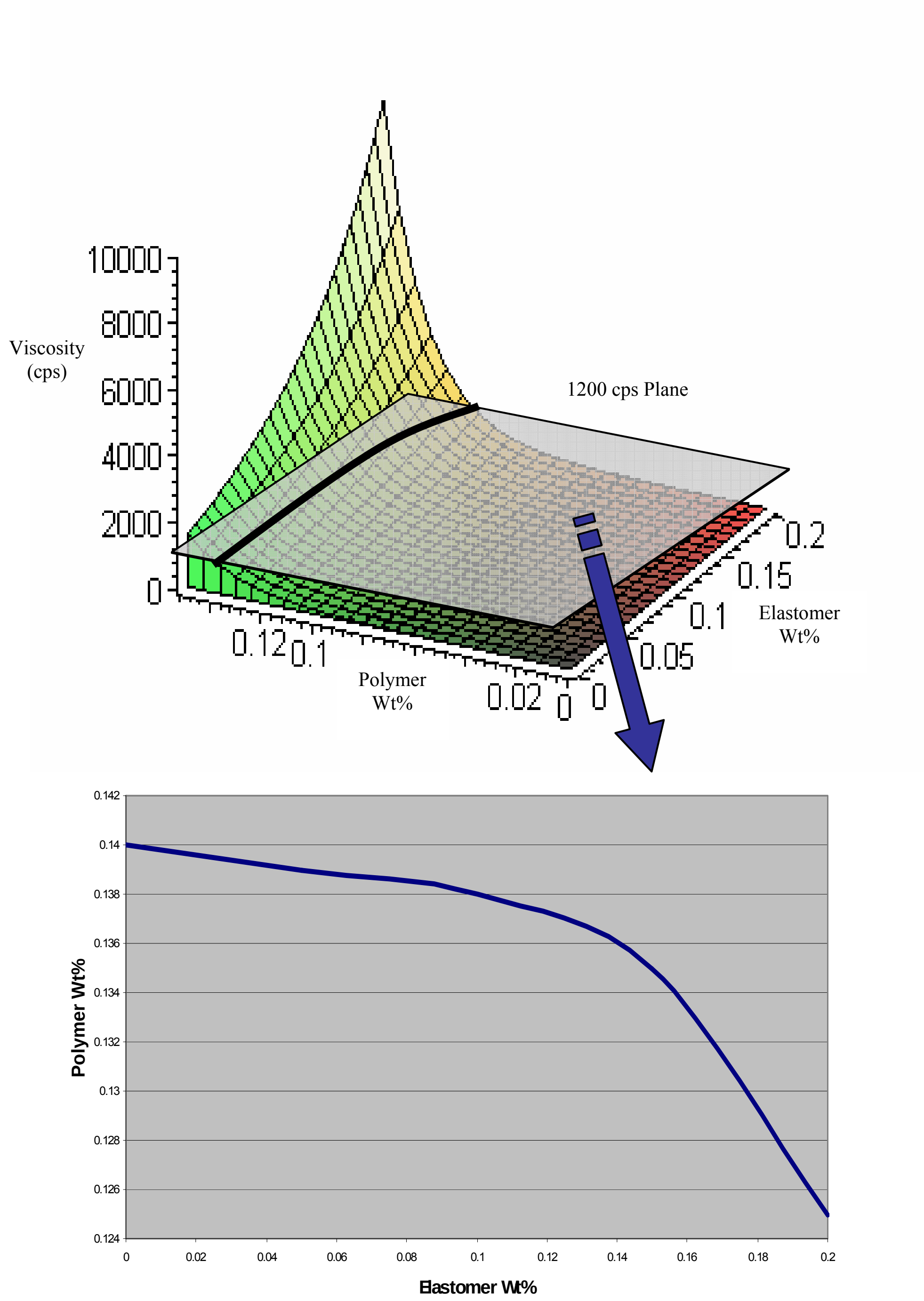


Figure 2.3-4. Formulation of Determining the Constant

2.5 Conclusion.

By employing novel model development techniques such as property integration and model decomposition; a complex product formulation development process to determine “cradle to grave” optimized behavior has been simplified. In this work, these methods were illustrated by addressing a problematic phenomenon in the nuclear power industry. The utilization of these modeling techniques took an industrial idea to full scale testing and production in under 18 months by reducing the number of subsequent laboratory trials.

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2.7 Acknowledgements.

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2.8 Disclaimer.

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CHAPTER 3 ANAEROBIC BIODEGRADATION TREATMENT OF WASTEWATER SOLUTIONS CONTAINING POLYVINYL ALCOHOL AND ASSOCIATED OXIDIZED CONSTITUENTS.

The unique attributes and material properties of polyvinyl alcohol (PVA) makes it an invaluable resource in the textile industry as a sizing agent, irreplaceable as an adhesive additive and has made it possible for new technologies in the waste minimization and hazardous material decontamination arenas. Because of the growing use of this and other water-soluble polymers, disposal processes of these products are being studied to maintain compatibility with the governmental regulations regarding organic constituent concentrations in wastewater streams suitable for discharge. This work focuses on the anaerobic digestion of wastewater streams that have been treated prior with a peroxide oxidation decomposition process. The data analysis in this article illustrates novel findings in the auto-inhibitory Haldane reaction kinetics associated with methanogenic anaerobic PVA disposal techniques discovered in the experimental procedures. This work was completed utilizing batch anaerobic biodegradation testing and volatile fatty acids determination by gas chromatography-mass spectrometry.

In the pages to follow, it will be shown that this project, submitted to the Journal of Water Environment Research, is a successful example of the evaluation of:

1) Polyvinyl Alcohol.
2) Methanogenic Anaerobic Digestion.
3) Peroxide Oxidation.
4) Effluent Process Wastewater.
5) Haldane Auto-inhibitory Reaction Kinetics.

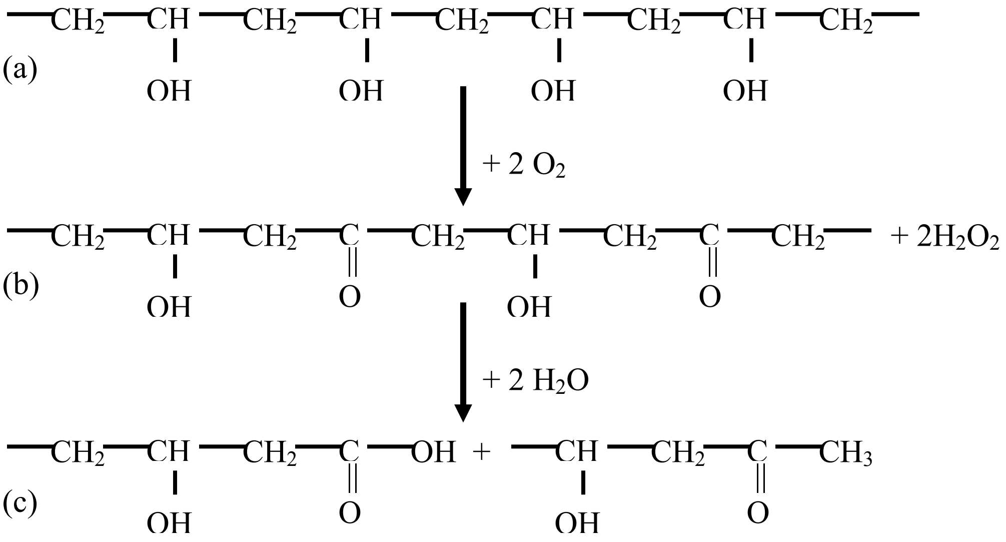
3.1 Introduction.

Current trends in the engineering community have moved to new technological advancements to overcome the increasing regulations regarding the disposal of industrial waste. Conservation, recycling, fuel blending, deep well injection and incineration are all costly alternatives that industry has been forced to implement. For example, the medical industry generates millions of pounds of waste each year, much of which is related to the use of disposable materials such as personal protective clothing and accessories necessary for patient care, which becomes contaminated and unsafe for further use. Likewise, the nuclear industry generates millions of pounds of waste that is classified as disposable products such as protective clothing, bags, mop heads, rags and other accessories. Much of this material is contaminated by tiny radioactive particles and difficult to remove, which dramatically increases the costs associated with burial or incineration. Other industries also generate waste streams with similar characteristics, and are in need of convenient and cost effective alternative to conventional waste disposal. (Steward, 2002)

The water-solubility and polymer fiber properties of polyvinyl alcohol (PVA) has allowed for an effective replacement for conventional fabrics used in these industrial situations where contamination is a possible health hazard. An example of this new generation of products is a water-soluble, PVA based surface decontamination product in the nuclear industry to replace the latex-based pealable films that have been used for many years. The new PVA coating serves to initially “fix” the contaminants in place for containment and ultimate disposal. Upon mechanical entrapment and removal, the polymer coating containing the radioactive isotopes can be dissolved in a solvent processor, where separation of the radioactive metallic particles occurs. Ultimately, only the collection of filtered solids from the contaminated PVA solution must be disposed of as nuclear waste. The ability to identify such a product creates a very attractive alternative to direct land filling or incineration and increases the cost efficiency of the entire decontamination process. In order for the polymeric film to be a viable candidate, it must be able to be disposed of easily and cost effective, which is the driving force in this investigation.

The direct discharging of the filtered PVA solution from the solvent processor is not plausible, even though there is no associated toxicity with the compound. The unaltered PVA in the waste solution will develop a “skin” formation at the liquid-air interface surface of the discharge body of water without immediate dilution. The PVA in the waste stream must be subjected to some form of chemical degradation to insure that the “skin” does not form and create an environmental hazard. The basic oxidative degradation scheme of PVA is shown in Figure 3.1-1.

The degradation of polyvinyl alcohol consists of two types of reactions: oxidation of the hydroxyl groups(Figure 3.1-1(a)) and cleavage of C—C linkages(Figure 3.1-1(b)). The degradation products include terminal carboxyl groups and methyl ketones. (Finch, 1992)



(a) $$-CH_2-\underset{OH}{\underset{|}{CH}}-CH_2-\underset{OH}{\underset{|}{CH}}-CH_2-\underset{OH}{\underset{|}{CH}}-CH_2-\underset{OH}{\underset{|}{CH}}-CH_2-$$

$$\big\downarrow + 2\ O_2$$

(b) $$-CH_2-\underset{OH}{\underset{|}{CH}}-CH_2-\underset{O}{\underset{\|}{C}}-CH_2-\underset{OH}{\underset{|}{CH}}-CH_2-\underset{O}{\underset{\|}{C}}-CH_2- \quad + 2H_2O_2$$

$$\big\downarrow + 2\ H_2O$$

(c) $$-CH_2-\underset{OH}{\underset{|}{CH}}-CH_2-\underset{O}{\underset{\|}{C}}-OH \ + \ -\underset{OH}{\underset{|}{CH}}-CH_2-\underset{O}{\underset{\|}{C}}-CH_3$$

FIGURE 3.1-1 General Degradation Reactions of Polyvinyl Alcohol.

3.1.1 Peroxide Oxidation/Ultraviolet and Ultrasonic Treatment.

Polyvinyl alcohol solutions that have been 90% mineralized with either hydrogen peroxide or potassium permanganate have been determined to not develop “skin” formations. (Oji, 2002) This same process can be achieved or improved with the addition of ultraviolet or ultrasonic treatment. The filterability and pumpability of the solution are also improved as the polymer chains in the solution are broken and viscosity decreases. However, this oxidation treatment creates large concentrations of organic acids and intermediate compounds as the polymer is broken apart piece by piece. These compounds cause the waste solution to have a high biological oxygen demand (BOD), which is a highly regulated measurement used to determine a discharged waste stream's possible impact on the ecosystem of the discharge body of water. Wastewater streams with excessively high BOD's are not allowed to be discharged and permitting will be denied by the city or state. Other means of breaking down the material must be determined.

3.1.2 Biodegradation -- Aerobic & Anaerobic Digestion.

Controlled respirometric assays of polyvinyl alcohol indicate that the PVA polymer compound may be completely degraded and organisms that consume PVA are viable in mixed culture activated sludge. The range of organisms able to complete this biodegradation and assimilate the PVA has been identified and studied in detail. (Finch, 1992) However, in the case of contaminated materials such as radioactive particles, it must be assumed that not all of the particulate will be extracted by the filter equipment and will accumulate in the biosolids waste layer of the water treatment vessel. In order to avoid creating large amounts of microbial yield and a new contaminated environmental hazard, this investigation will emphasize anaerobic digestion, which is characterized by low microbial yields.

In anaerobic systems, the reactions pathways illustrated in Figure 3.1-1 are accomplished in a similar fashion called methanogenises, where carbon dioxide acts as the electron acceptor in place of the oxygen, thereby producing methane. Because these anaerobic degradation processes tend to be governed by slow reaction kinetics, the only economically feasible plant configuration that can treat the large volume of produced wastewater is a combinational approach of a secondary biodegradation step following a primary chemical oxidation process. This peroxide treatment alleviates the skin formation phenomena, increases the pumpability of the liquid, improves the polymer solubility characteristics and reduces the size distribution of polymeric particles.

3.2 Experiment Methodology.

The first experimental process step is to prepare a >90% mineralized/oxidized PVA solution using concentrations seen in industry from solvent processing equipment. (Approximately originally 8-12% PVA by weight) A Stociometric amount of hydrogen peroxide is added and the solution is tested for oxidation extent by a process developed by Air Products to determine stable PVA extraction from paper. This colorimetric testing technique is outlined by Hanson (1998). Additional hydrogen peroxide is added until the solution reaches a >90% oxidized state. This process produces an effluent with a measurable BOD range of greater than 2000 parts per million (ppm) and less than 2500 ppm.

3.2.1 Batch Anaerobic Biodegradation Testing.

Anaerobic batch reactors were fabricated from one-liter capacity serum bottles with teflon coated septa and teflon stirrers. The reactor contents were mixed using light-duty magnetic stir-plates and internal teflon coated stir-bar. There was approximately 400 mL of headspace when operated with 600 ml of aqueous content. An off-gas lime was attached through the septum using a large-bore needle. The off-gas was bubbled into an open bottle of water to prevent atmospheric oxygen to enter the reactor. Reactor contents were sampled though a second access line using a 10 ml syringe.

Anaerobic biomass was obtained from an industrial anaerobic reactor treating foul condensate at a paper mill. The biomass was thickened (7,300 mg/L) and 100 mL (730 mg) of biomass was added to 500 mL of PVA wastewater. The resulting solution had a biomass of approximately 1,220 mg/L. Aliquots of the reactor contents were removed periodically for VOA analysis by GC/FID.

3.2.2 Volatile Fatty Acids by Gas Chromatography.

An Agilent 6890 gas chromatograph with a split/split less injection port (split ratio 1:1) using a helium carrier gas at a temperature of 250oC (482oF) and an inlet pressure of 34.13 kPa (4.95 psi) was used to measure the VOAs. The column was an HP-FFAP (free fatty acid phase) with dimensions of 15 meters length x 0.32 mm I.D. x 0.25 um film thickness. The carrier velocity was 25 cm/sec (flow rate of 2.4 cc/min). A flame ionization detector was used with a temperature of 250^{o}C, hydrogen flow of 40 ml/min, air flow of 450 ml/ in, and a makeup flow of 45 ml/min helium. A pulsed split less injection with a total volume of 5 µL was used for standards and samples.

Individual compound standards were prepared for acetic, propionic, butyric, isobutyric, valeric, isovaleric, and caproic acid. The volatile organic acid standard compounds were purchased from Sigma Chemical Co. A four point standardization was employed using standards fresh aqueous solutions containing 5,000 mg/L, 500 mg/L, 50 mg/L, and 5 mg/L of each compound.

3.3 Results & Discussions.

The outlined experimental procedure generates a textbook example of substrate inhibition kinetics in wastewater treatment. Figure 3.3-1 illustrates this phenomenon by providing the biological oxygen demand (BOD) removal rate at varying concentrations of PVA contaminate substrate concentrations. It can be seen that high concentrations of substrate inhibit the reaction kinetics.

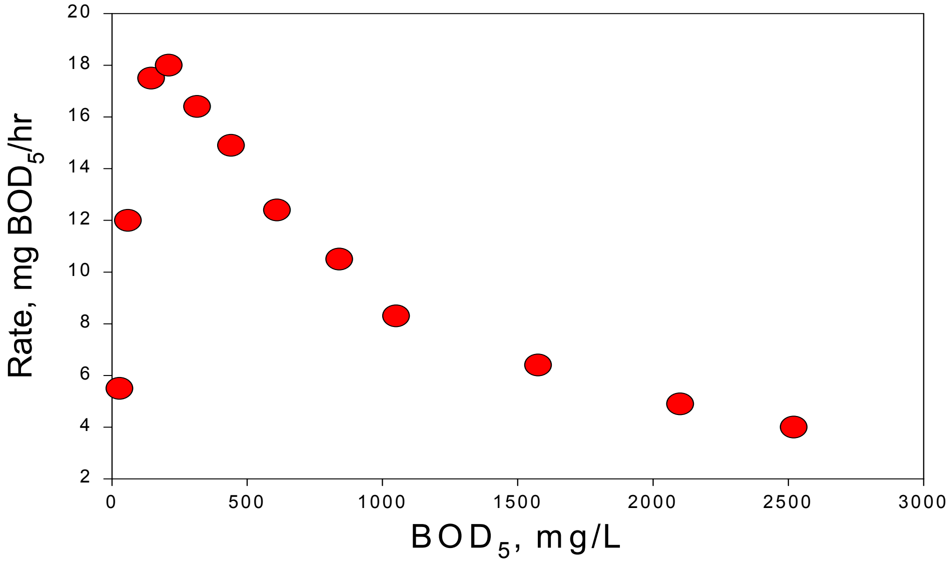


FIGURE 3.3-1 BOD Removal Rate of PVA Oxidized Constituents by Anaerobic Digestion.

The experimental data analysis also confirms the assumption that the anaerobic degradation pathways of the substrate occurs by Methanogenises. Figure 3.3-2 illustrates the gas production of the wastewater treatment system. Methane is the primary effluent gas produced.

Further evaluation of this data allows for the assembly of kinetic models to accurately describe the reaction behaviors. The results of this experiment illustrates a classic example wastewater treatment behavior where a maximum removal rate is reached and further increase in substrate concentration BOD's inhibit the microbial action and leads to a decrease in rate. The data behavior is best illustrated by the Haldane substrate inhibition model for biological kinetic expressions for cell synthesis in the form:

Equation 3.3-1

$$k_H = \frac{k}{1 + (K_S/S) + (S/K_I)}$$

where k is the substrate removal rate constant(hr^{-1}), K_s is the ½ velocity constant(mg/L), which is defined as the concentration at which ½ of the maximum rate is achieved, S is the substrate concentration(mg/L), and K_I is the inhibition controlled constant(mg/L).(Sundstrom, 1979) Figure 3.3-3 demonstrates the integration of this model with the generated experimental data.

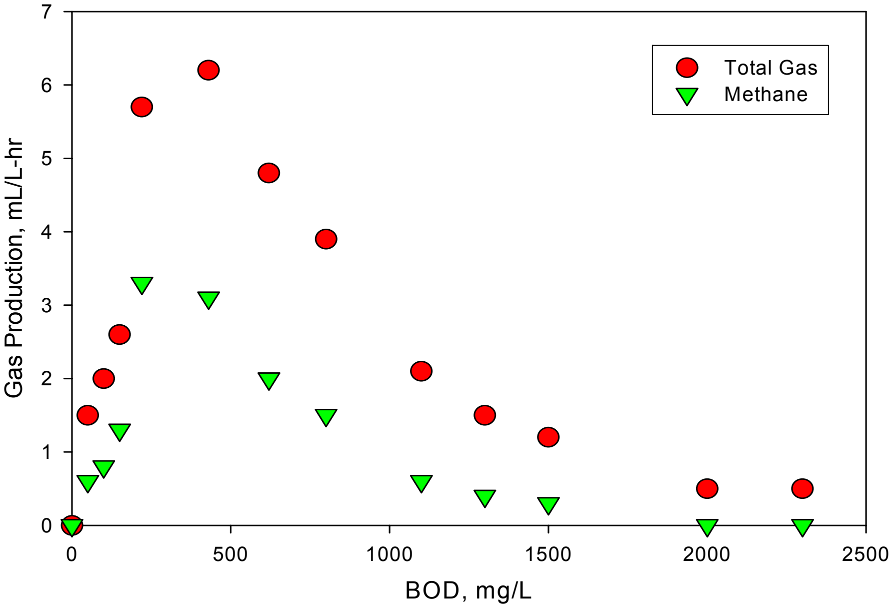


FIGURE 3.3-2 Gas Production Rates of PVA Oxidized Constituents During Anaerobic Digestion.

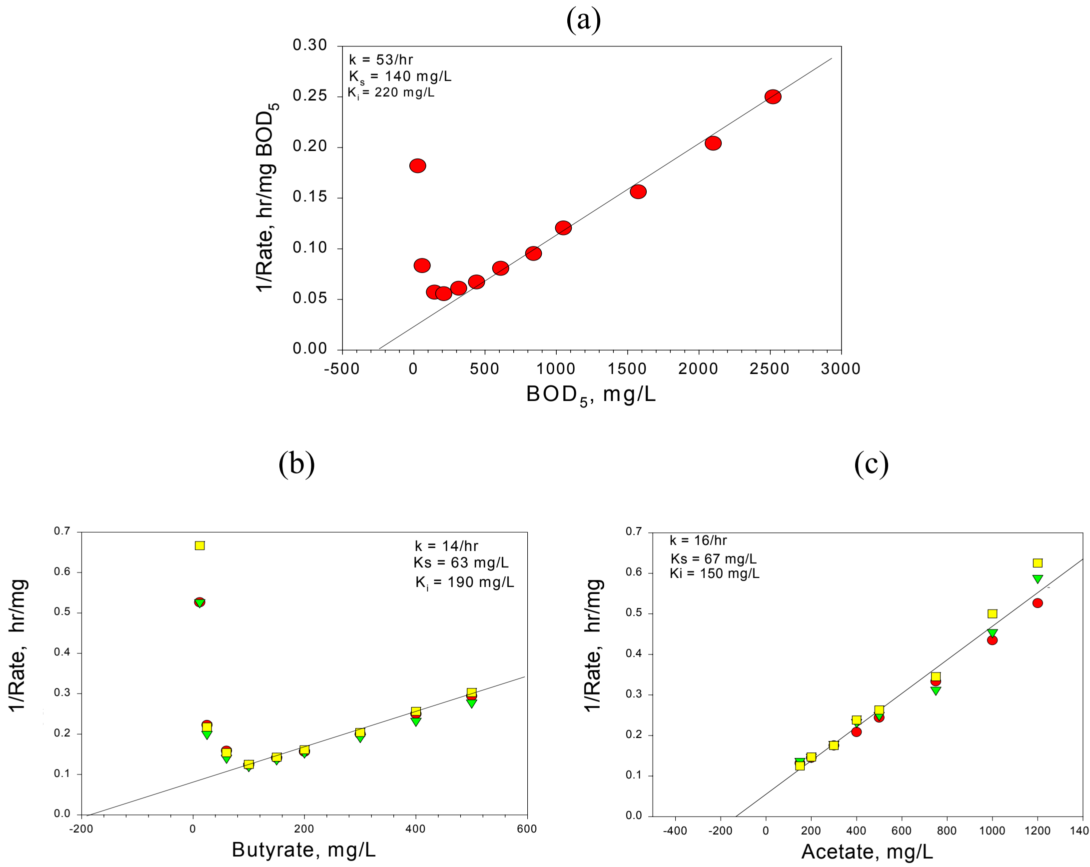


FIGURE 3.3-3 Haldane Substrate Inhibition Kinetics Model for Oxidized PVA Constituents for Anaerobic Digestion. (a)Overall BOD (b)Butyric Acid (c)Acetic Acid

The model constants k, Ks and KI where determined to be 53hr^{-1}, 140 mg/L and 220 mg/L respectfully for the overall BOD degradation model. Figures 3.3-1 and 3.3-3(a) also show that the overall removal rate of BOD reaches a maximum at approximately 200 mg/L and decreases dramatically with increasing BOD concentrations exceeding the 200 mg/L value. It was determined that the measured BOD of the substrate was mainly comprised the concentrations of Acetic and Butyric Acid. The Haldane model constants were also calculated for Butyric and Acetic Acid and are provided in Figure 3.3-3(b) & (c). With the proper kinetic model structure and process behaviors explained, it is possible to develop wastewater treatment simulations to aid in determining wastewater equipment configurations, sizes and multiple tank systems. Figure 3.3 demonstrates the dynamic substrate concentration in a batch-wise treatment scenario.

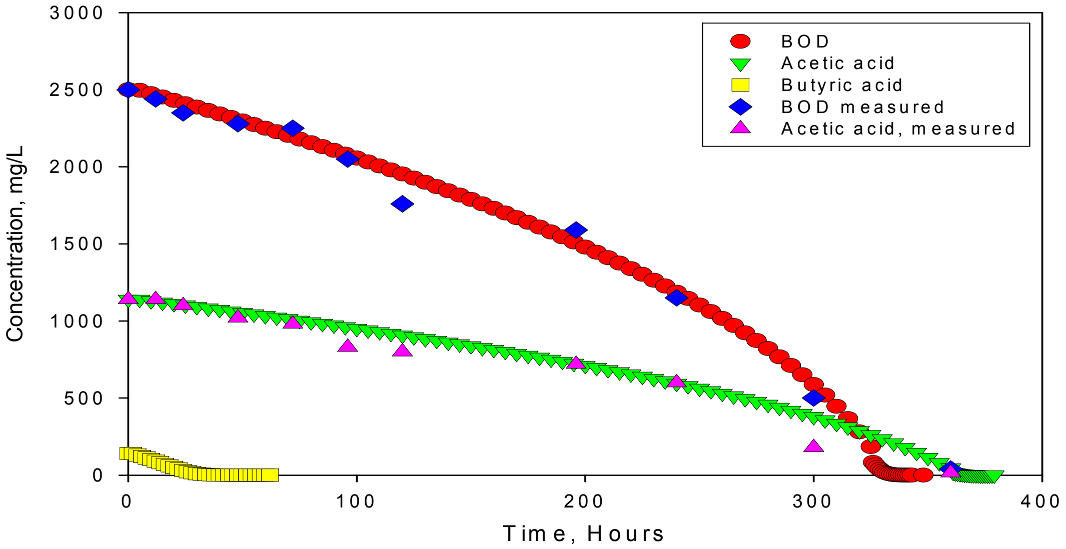


FIGURE 3.3-4 BOD Concentrations in a Batch Treatment Reactor for Oxidized PVA Constituents for Anaerobic Digestion.

Because the BOD of this system is made up of primarily two organic compounds, Acetic and Butyric Acid, the substrate in the reactor begins with an initial concentration of 2500 ppm. Figures 3.3-3 and 3.3-4 not only shows the time required for waste decomposition, but also the shared trend decline in Acetic Acid, Butyric Acid and BOD. Both the model and measured values are reported. The system is able to remove the BOD to the effluent regulation discharge level in 325 hours in a batch treatment reactor. The performance of the wastewater treatment system in a continuous feed stirred tank reactor configuration was also investigated and is provided in Figure 3.3-5. This figure exhibits the slow inhibitory kinetic effects of the wastewater system. The effluent BOD concentration in the time less than 130 hours is decreasing very slowly and controlled by the rate limiting Haldane kinetics. At 130 hours, the critical residence point is reached where the biomass growth rate has allowed for the accumulation of organisms to reach the proper concentration ratio of substrate to biological agents. The degradation rate at the critical point dramatically increases and the reaction rapidly accelerates. The final effluent discharge concentration of BOD is attained with a 200 hour hydraulic residence time.

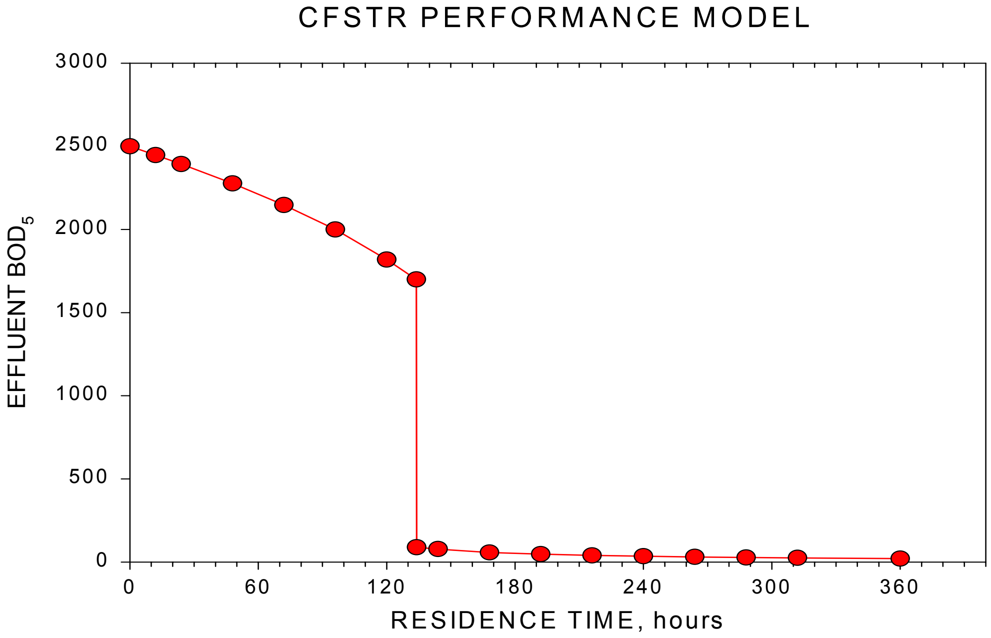


FIGURE 3.3-5 BOD Concentrations in a CFSTR Treatment Reactor for Oxidized PVA Constituents for Anaerobic Digestion.

3.4 Conclusions.

This experimental work has outlined the primary kinetics involved in the anaerobic wastewater treatment of a process stream enriched in an oxidized water soluble polymer. PVA and PVA oxidized constituents are biodegradable under strictly anaerobic conditions, which is evidenced by the methanogenic pathway data obtained by this experiment. This process is rate limited by Haldane inhibitory kinetics at BOD concentrations greater than 200 ppm, which is comprised of organic compounds primary made up of Acetic and Butyric Acids formed during the industrial peroxide oxidation procedure. Due to the volume of most plant-wide operations, the use of batch water treatment facilities to remove water-soluble polymer constituents from wastewater streams will be limited, even though it achieves the best overall BOD removal. The more logistical wastewater treatment facility configuration consists of a series of continuous feed stirred tank reactors with an overall resonance time of approximately 200 hours. The design of the system to operate at different optimum bulk concentrations will reduce the effective resonance time; however, this system will have to use complicated batch-wise start-up procedures.

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3.6 Acknowledgements.

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CHAPTER 4 ACADEMIC CONSULTING: NOVEL ADVANCEMENTS IN THE CURRENT TREND OF INDUSTRIAL WASTE REDUCTION AND TRANSFERRING THESE TECHNOLOGIES FROM THE PLANT FLOOR TO THE CLASSROOM.

One of today's most difficult challenges in technology-based curriculums is the integration of real world examples that will familiarize students with occupational environments and tasks. New methods of identifying, analyzing, presenting, and familiarizing students with these examples illustrate the use of the academic concepts and theory in current industrial practice. This work addresses the growing concern of the associated costs of waste contamination, removal and governmental regulation compliance in manufacturing industries. Conservation, recycling, fuel blending, deep well injection and incineration are all costly alternatives that industry has been forced to implement. Current trends in the engineering community have developed new technological advancements to overcome the increasing regulations regarding the disposal of industrial waste. New process and product optimization techniques are proposed, implemented, and illustrated in three separate studies to promote the creative nature of student thinking and problem solving in complicated technological systems and promote the integration of real world issues with academic theories in science, math, engineering and technology education. This work has been submitted to the Journal of Science, Math, Engineering, and Technology Education: Innovations and Research.

4.1 Introduction.

The Auburn Engineering Technical Assistance Program (AETAP) is a coalition of Samuel Ginn College of Engineering departments partnering with Alabama Cooperative Extension System (ACES), National Science Foundation, College of Business, and other research and government establishments which focus on the needs of Alabama's manufacturers. The primary objective of AETAP is to facilitate the transformation of knowledge from Auburn University into innovations that will create new wealth and strengthen Alabama's economy. AETAP provides manufacturers with high quality technical assistance, technology transfer and workforce training. Under this research consortium, a multitude of successful industrial projects have been completed. The technological achievements made from this work have been published in a number of scientific journals; however, the academic curriculum advancements made possible by this work have remained obscured. The knowledge transfer does not stop at only the faculty and students directly involved with the case study, as classroom discussions and projects replicate the troubleshooting skills gained on the plant floor. These optimization processes and the associated benefits are illustrated in three separate case studies in the chemical engineering research and development arena.

4.1.1 Product & Process “Cradle to Grave” Optimization Theory.

In the hazardous material management and governmental regulation compliance fields, there is a concept known as “cradle to grave” liability for hazardous materials producers. The Resource Conservation and Recovery Act (RCRA) of 1976, which amended the Solid Waste Disposal Act, was the first substantial effort by the United

States Congress to establish a regulatory structure for the management of solid and hazardous wastes. This set of regulations yielded a complex assortment of regulations governing the management of hazardous waste from the cradle to the grave. Specifically, Subtitle C of RCRA addresses this "cradle-to-grave" concept and the associated requirements for hazardous waste from the point of generation to disposal. Even though process design and product formulation rarely has anything to do with hazardous material development, our optimization technique adopts a similar concept and the name, maximizing all the product behaviors between development and disposal.

Typical product development and the associated processing systems in industry generally occur in three separate stages; formula creation, production design and waste management. Not only do different groups of chemists, engineers and scientists generally conduct these three stages of construction, but also different companies and institutions. New products are formulated in laboratory experiments to improve on existing industrial niches or to create completely new markets. These formulas are optimized to produce the best possible product behavior and quality in order to maximize marketability and profitability. This product recipe is then passed on to the process development researchers to determine the optimized manufacturing system of equipment, chemistry and fabrication methods. It is not uncommon to outsource production to entirely different companies, which can separate the goals of product creation and process equipment usage. Even though this network of equipment is also optimized with consideration to production rate, manufacturing efficiency and corporate profitability, the optimized product train is limited to processes that only produce the independently optimized product formula. The combination of the product formulation and manufacturing process creates an entirely new system that must be optimized. Even though the formula and process are considered optimal, because they were determined independently from one another, the overall system may not be at the peak of working conditions. Because of non-linearities in chemistry, thermodynamics and mechanics, small changes in product formula may relate to drastic changes in the production requirements and vise versa. In the case of products that are not completely consumed or create byproducts, the waste and refuse treatment processes creates another process associated with the formula. A separate company or institution generally conducts this process, whether it is water treatment, recycling, destruction, or land filling. As in the production process, small changes in the formula can create drastic changes in the waste management aspects of the product. These independent process optimizations are illustrated in Figure 4.1-1(a).

With the increasing pressure of reducing contaminate regulations of waste streams, new techniques of maintaining governmental compliance must be developed. By applying the concept of “cradle to grave” responsibility to product formulation, a reduction in measured effluent parameters can be achieved. This is accomplished by optimizing the product formulation and production process concurrently to reduce the amount of associated byproduct that must be disposed of. By optimizing the product formula, process parameters, and disposal procedures simultaneously, shown in Figure 1(b), the entire system produces acceptable product behaviors, maximum manufacturing process profitability and efficiency, and minimum waste impacts and costs. In order to access the full benefits of this product system optimization, novel modeling techniques must be employed to predict the severe non-linearities in the product performance throughout the life cycle. It is type of creative and cost effective problem solving skills that must be taught to new generations of environmental scientists and engineers. Classroom examples are presented for evaluation and discussion.

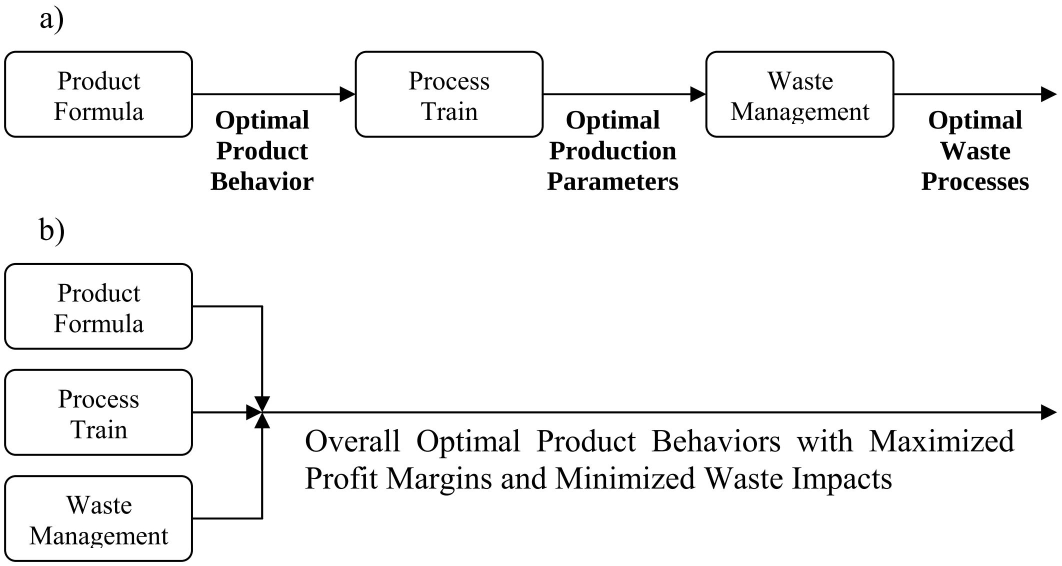


Figure 4.1-1 Process Optimization Techniques.
a) General Formula Development and Manufacturing Process Optimization Practice
b) "Cradle to Grave" Optimization

4.2 Case Study I. The Design and Implementation of a Model Predictive Cascade Control Scheme for a Vacuum Drying Process.

Resource Innovations is a specialty chemical manufacturer producing accelerators for polymers, rubber and latex including thiuram disulfides, dithiocarbamates, xanthogens, and activated liquid dithiocarbamates. They decided to construct a process of producing Zinc Alkalate, a monomer used in the construction of golf balls. The task of designing and implementing an adequate automation and control system for this process that would fulfill governmental regulations was brought to the Auburn Engineering Technical Assistance Program (AETAP). This chemical process can be divided into two separate, but equally important stages.

The first stage is an exothermic batch reaction of Zinc Oxide and Acrylic Acid. This reaction takes place in a steam-jacketed reactor seen in Figure 4.2-1 in the presence of hexane in order to promote the reaction kinetics by providing a liquid media for the reaction to take place. Hexane is listed as a priority air pollutant under the EPA Title V Air Permit and National Emission Standards for Hazardous Air Pollutants (NESHAP/HON) regulations. Under these regulations, it is required to minimize and monitor yearly solvent losses to ensure that no more than 10 metric tons of material is lost in any 365-day period.

The second and more complicated stage is the vacuum drying removal of hexane and water produced in the reaction seen in Figure 4.2-2. This stage has the greatest potential for solvent loss and it is extremely important to optimize this process step from both an environmental and economical standpoint. The overall processed product of these two stages is a dry white solid with a consistency comparable to baby powder.

Figure 4.2-1 Vacuum Dryer.

Figure 4.2-2 Batch Reactor.

The controller was connected to a personal computer and therefore a human machine interface (HMI) had to be developed. This control panel was created and is run by a software package sold by Allen-Bradley known as Rockwell Software. This package contains ladder logic programming, display technology, and data analysis capabilities required to control the extensive network of actuated and control valves, pumps, agitators, control parameters and conveyers necessary to properly operate both process stages simultaneously. Inventory levels, temperatures and pressures of the tank farm were also desired to be observed continuously by the HMI. In order to accomplish this, digital inputs (on or off signals) are monitored using two Allen-Bradley 1746 NI-16I, 16 channel input boards.

The analog inputs (measured signals) are read by Allen-Bradley 1746 IB-8, 8 channel input cards. Likewise, an Allen-Bradley 1746 NT-8 thermocouple input card reads the analog temperature signals. Output signals are generated by either an Allen Bradley 1746 OA-16(digital) or 1746 NO4I (analog) card depending on the signal type required. A K-Tec Level Transmitter and float inside each tank transmit all level information as a 4-20 milliamp signal. All temperatures are determined using thermocouples or Resistance Temperature Devices (RTD). DP cells (Differential pressure transmitters) provide pressure data while flow meters obtain volumetric flow data. All of the equipment described above is necessary for the successful control of the optimized ZDA process.

4.2.1 Control Installation.

The physical installation of the instrumentation required a few weeks of intensive labor. The majority of the tanks, piping and pumps were already in place prior to the instrument installation, which made intergrading the new equipment even more complex.

The wiring of the instrumentation was an iterative process as each piece of equipment works differently with the controller cards. This collaboration of electrical behavior and chemical concepts is generally beyond the scope of the curriculum of any one specialized engineering program. This type of plant floor problem solving example is exactly what this research is designed to identify and present in the classroom. For example, a thermocouple works on the principle that resistance in the probe changes as a function of temperature. Once a 24-volt power supply is wired in parallel with the thermocouple, the probe will restrict the amperage in the negative wire exiting the device. The card installed in the controller measures this amperage in a series-wiring configuration. This circuit also must include a digital display to back up the read-out on the HMI in case of a computer malfunction. This creates another interesting example for classroom discussion. The integration of the digital displays could cause errors in the controller if the wiring is not correctly installed. The dual measuring devices must be wired in parallel with each other or else the internal resistance of the display will interfere with the resistance of the temperature probe and cause the card reading to be inaccurate.

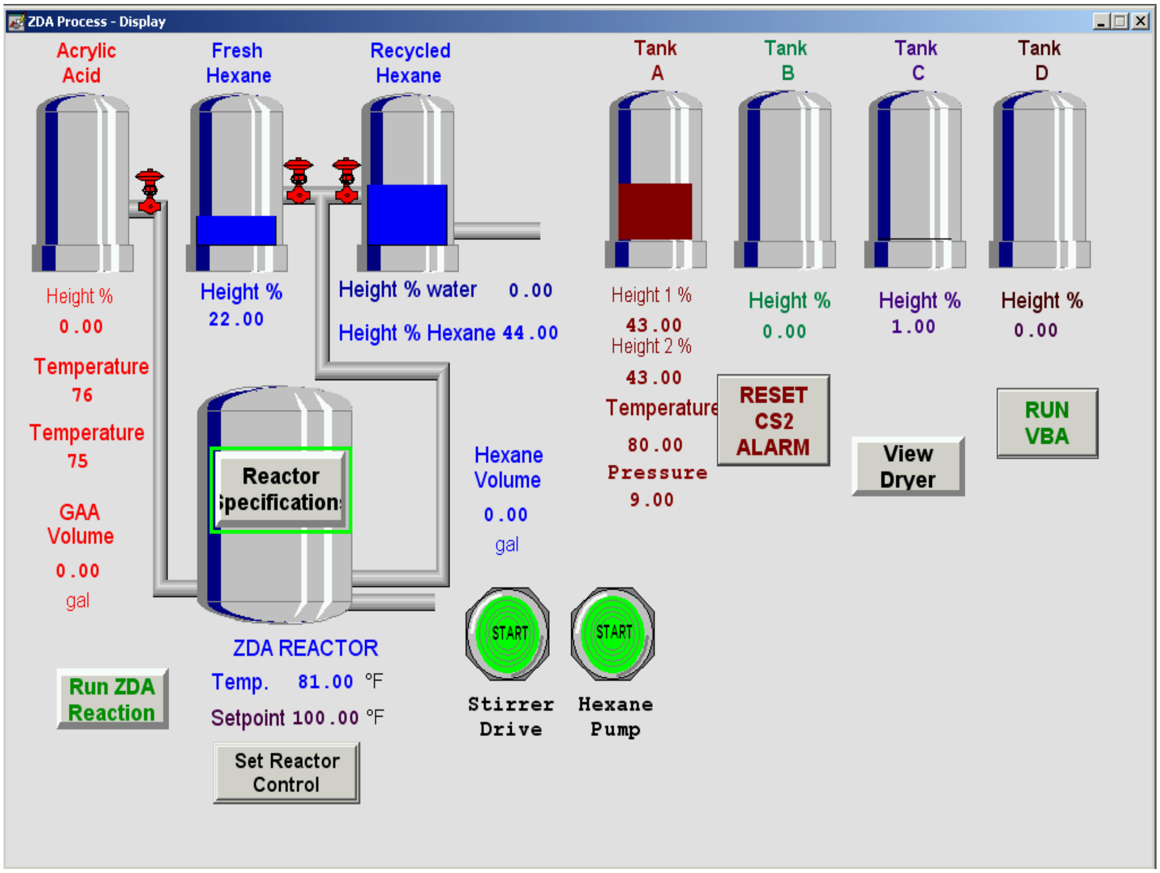
This type of industrial example is invaluable as it stresses the thinking and problem solving skills rather than a right or wrong scenario because, under different circumstances, this wiring technique is not effective. For example, in order to maintain dual display capability on the circuit for an RTD, an individually powered display that produces a second 4-20 milliamp signal is required. Flow meters also necessitate a special digital display in order to allow dual measurements.

Once the instrumentation was properly installed and the processor and computer were receiving signals, all analog channels were calibrated. This, like the wiring, involves an iterative learning process not taught by any textbook. No two pieces of measuring devices were calibrated in the same manner. Vendor information and operating manuals were studied in order to determine calibration techniques to insure proper functionality.

4.2.2 Human Machine Interface.

The controller itself had to be intergraded into the already functioning computer network system of the plant. Once the network Ethernet connection was correctly installed and the instrumentation was properly communicating with the controller (and therefore the computer), an effective display was created to express process data. A number of important design parameters had to be met to ensure proper plant operation. It was desired that both processes must be able to run simultaneously, even though they are under the control of different screens. The tank farm data must also be expressed on both screens in order to insure continual monitoring.

The reaction control screen (Figure 4.2-3) is comprised of both animated displays of the reaction process and the tank farm data. Onscreen switches, inputs and buttons allow the operator to open actuated valves, start the reactor agitator, activate loading pumps, change control parameters and set points, initiate the reaction process and manage the alarm systems.



Acrylic Acid: Height % 0.00; Temperature 76; Temperature 75; GAA Volume 0.00 gal

Fresh Hexane: Height % 22.00

Recycled Hexane: Height % water 0.00; Height % Hexane 44.00

Hexane Volume 0.00 gal

Tank A: Height 1 % 43.00; Height 2 % 43.00; Temperature 80.00; Pressure 9.00

Tank B: Height % 0.00

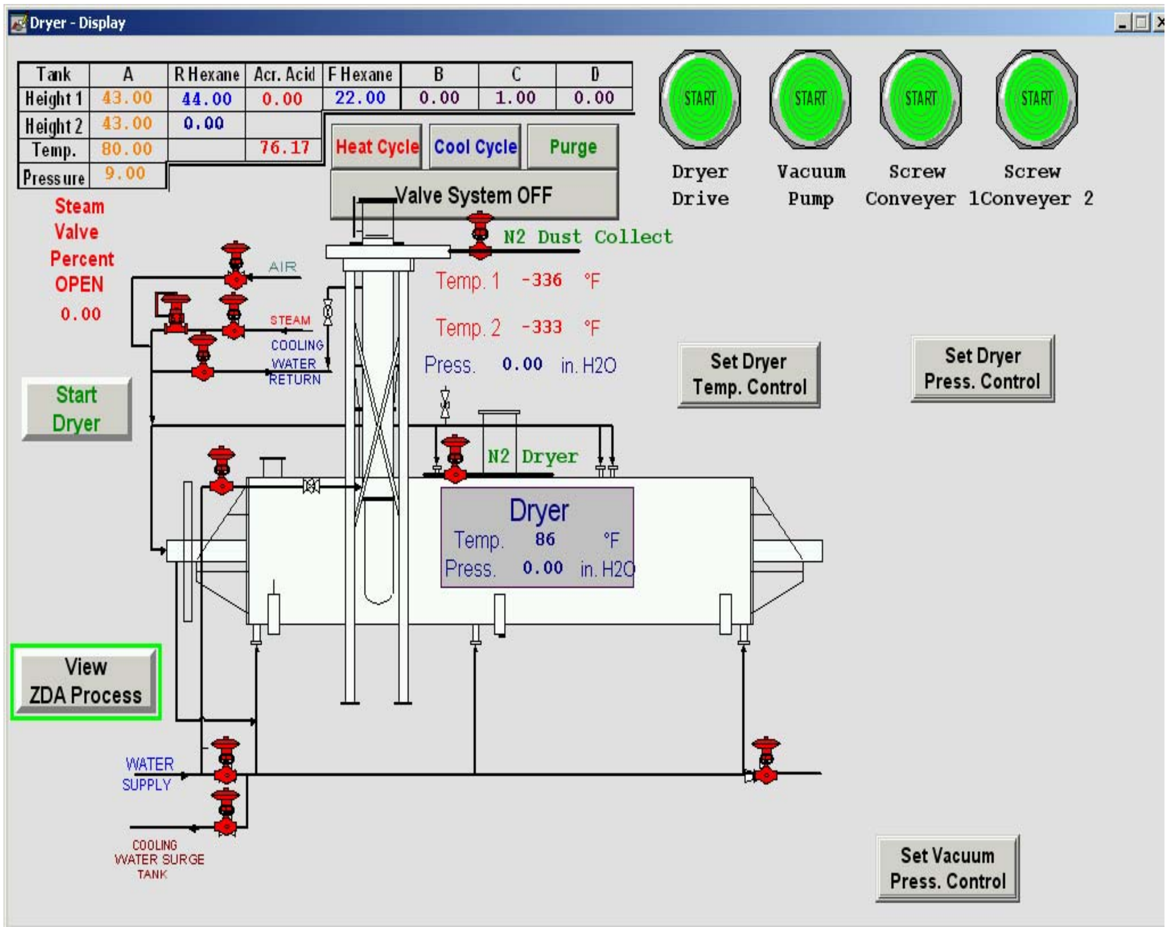
Tank C: Height % 1.00

Tank D: Height % 0.00

ZDA REACTOR: Temp. 81.00 °F; Setpoint 100.00 °F

Figure 4.2-3 Reactor Human Machine Interface.

The dryer control screen (Figure 4.2-4) consists of an active database listing all of the tank farm data to allow level, temperature and pressure monitoring to continue while the dryer is in operation. Animated displays, switches and buttons permit the use of multiple systems to be used on the dryer effectively. A network of actuated valves are opened and closed to permit cooling water, heating steam, and pressurized air to enter the dryer's jacket during different operations of the process. The HMI that controls this complex maze of piping with one button operation. Other HMI display controls start the drive motor of the stirrer, initiate the vacuum pump system, manage the temperature, pressure and vacuum controls, regulate the nitrogen purge valves, and operate the screw conveyers for unloading the product.


Dryer - Display

Tank	A	R Hexane	Acr. Acid	F Hexane	B	C	D
Height 1	43.00	44.00	0.00	22.00	0.00	1.00	0.00
Height 2	43.00	0.00					
Temp.	80.00		76.17				
Pressure	9.00						

Steam Valve Percent OPEN 0.00

Temp. 1 -336 °F

Temp. 2 -333 °F

Press. 0.00 in. H2O

Dryer

Temp. 86 °F

Press. 0.00 in. H2O

Figure 4.2-4 Dryer Human Machine Interface.

Pressing a linked onscreen button switches from one interface screen to another. Both control displays remain active at all times which allows both processes to continue independently of one another.

4.2.3 Control Design Philosophy of the Reaction Process.

The reaction of this process is classified as an instantaneous exothermic reaction. The best control scheme of this form of elementary kinetics is accomplished by varying the addition rate of the limiting reactant using a control valve. In this particular project, an air-driven diaphragm pump is used in place of the control valve. This is an acceptable substitute because pumps of this type work similar to control valves. As air is supplied to the pump by a current to air transducer, the pump regulates the flow rate of liquid being delivered to the reactor. A PI control algorithm was built into the ladder logic programming and was designed and downloaded into the controller to manage the air supply to the pump. The controller gain and time constant for this equation can be manipulated to optimize operation of the reaction from the corresponding HMI. The optimal values of these variables are determined by examining reactor data that the computer automatically logs from previous reaction cycles.

4.2.4 Control Design Philosophy of the Drying Process.

The drying process is more complicated and therefore is much more difficult to control. The release of hexane into the atmosphere is to be minimized in order to meet air-permitting regulations and to lower production costs. To accomplish this, a cascade controller format is designed to maximize heating, while maintaining minimal hexane emissions. The dryer is first evacuated of air by a vacuum system.

A PI controller manages this vacuum system illustrated in Figure 4.2-5, by manipulating a vacuum bypass valve. A desired vacuum pressure is entered into the HMI and this value is maintained by varying the flow of air allowed to enter the vacuum line entering the pump. Once the desired vacuum is reached and reaches a steady state, the bypass valve is locked in this position and the heating process begins. It is most economical to raise the temperature of the inside of the dryer to slightly below the boiling point of hexane. As the vapor pressure of hexane is reached a larger amount of vapor is present in the vessel, increasing the pressure. This pressure manipulates the temperature set point and lowers the heat energy entering the dryer and restores the vacuum pressure to the set point. Likewise, when the pressure decreases, the cascade control reacts by increasing the temperature and maximizing the hexane evaporation.

Figure 4.2-5 Vacuum Pump System.

4.2.5 Conclusion.

This project is a successful example of academic knowledge and industrial know-how and illustrates the creative and cost effective problem solving skills vital to successful engineering careers. The governmental regulations governing this process and the associated contamination concerns were fulfilled by using computer control technology to minimize the possibility of solvent losses while automating the required documentation and paperwork procedures. This system was developed by optimizing the entire process, identifying sources of environmental release and creating an innovative control system to minimize the process drawbacks. This case study is a perfect example of engineering theory and technology, tested under fire, are effective once properly intergraded into the private sector industrial environment.

4.3 Case Study II. A Novel Systematic Approach for Synthesis of Optimal Polymer Films for Radioactive Decontamination and Waste Reduction.

Orex Technologies, Incorporated, produces and sells disposable polymer products such as protective clothing, gloves, shoe covers and specialty items for the nuclear power industry. In this research, effective and systematic models were developed to synthesize the optimal formulations for explicit engineering applications in the nuclear industry, i.e. radioactive decontamination and waste reduction. The majority of this work involves the development of a polymer matrix that is applied to surfaces as part of a decontamination system. The polymer coating serves to initially “fix” the contaminants in place for detection and ultimate elimination. Upon mechanical entrapment and removal, the polymer coating containing the radioactive isotopes can be dissolved in a solvent processor, where separation of the radioactive metallic particles can take place. Ultimately, only the collection of divided solids must be disposed of as nuclear waste. By conducting this research, an attractive alternative to direct land filling or incineration was found by conducting testing and optimization of the disposal process equipment. This philosophy provides waste generators a way to significantly reduce waste and associated costs, and help meet regulatory, safety and environmental requirements.

4.3.1 Model Development Methodology.

Formulation of new products and improvement of existing merchandise is practiced in many different industries including paints and dyes, polymers and plastics, foods, personal care, detergents, pharmaceuticals and specialty chemical development. Current trends in the engineering design community have moved towards the development of quantitative integrated solution strategies for simultaneous consideration of multiple product characteristics. The optimization variables are most often determined by qualitative attributes, stochastic variables, visual observations and/or design experience. The effectiveness of these approaches is limited by available data, bias towards specific solutions, reproducibility, and experimental error. Model insight is required for development of fast, reliable and systematic screening methods capable of identifying optimal formulations and reducing the number of subsequent laboratory trials.

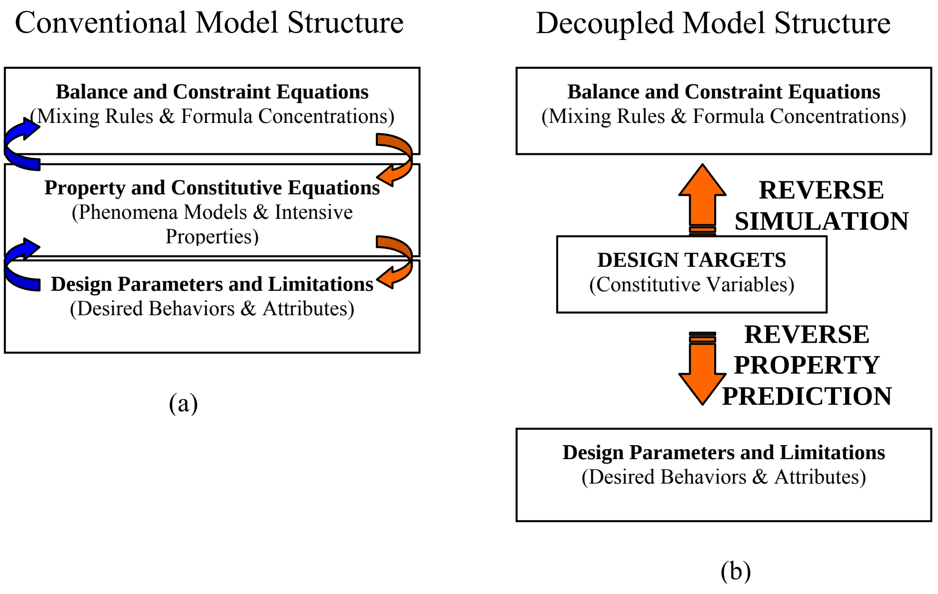
In order for the product to exhibit the desired performance, a combination of discrete constraints must be fulfilled. Identification of an optimal formulation that is suitable for the desired system requires integration of all the interlacing behaviors of the product constituents. These characteristics include the constituents used for construction as well as their inherent properties. This is accomplished by using a combination of novel modeling techniques.

4.3.2 Product Formula Model.

The desire to decontaminate surfaces inside nuclear power plants has been addressed with a number of different products. The implementation of latex-based pealable films has been used for many years. The coating serves to initially “fix” the contaminants in place for containment and ultimate removal. However, power plants have discontinued the use of these products because of their long drying times and expensive disposal costs. In the place of these products, protocol has turned to the use of steam jets to remove the radioactive particles and clean the exposed surface. This method has proven to be ineffective due to a build up of contaminants that, through molecular transport, become airborne and contaminate larger areas. The purpose of this work is to develop an effective and systematic model to synthesize a formulation of a water soluble polymer film coating for radioactive decontamination and waste reduction. This material development involves the use of a polymer matrix that is applied to surfaces as part of the decontamination system in place of the past latex products. Upon mechanical entrapment and removal, the polymer coating containing the radioactive isotopes can be dissolved in a solvent processor, where separation of the radioactive metallic particles occurs. Ultimately, only the collection of filtered solids must be disposed of as nuclear waste. The ability to identify such a product creates an attractive alternative to direct land filling or incineration. In order for the polymeric film to be a viable candidate, it must exhibit the desired performance that previous coatings are unable to. These characteristics include, drying time, storage constraints, decontamination ability, removal behavior, application technique, coating strength and dissolvability processes.

The first step in developing this “cradle to grave” model is property integration. This method consists of tracking functionality instead of chemical species in order to represent the synthesis problem from a property perspective. The conventional approach to product formulation development is selecting constituents that exhibit desired produced properties and optimizing the mixing ratios. In order to model the product characteristics, these pre-determined candidate components are required as inputs to the design algorithm. These input choices are based on qualitative process knowledge and/or design experience, which can exclude solutions involving other possible raw material sources. This modeling approach allows for solution of many different engineering problems to be conducted on a property only basis. This method allows for identifying optimized solutions to specified chemical engineering problems by determining the desired output and solving backwards for the constituents and compositions. By employing this technique along with a model decomposition technique, the complexity of solving for both non-linear solutions to composition and behavior is separated into two separate, less complex models.

These modeling techniques are useful tools to reduce the complexity involved when trying to simultaneously optimize balance and constraint equations with constitutive and property models. Although this procedure was created for process development, minor changes allow for application to product design. The main objective of this process is to separate the balance and constraint equations from the often complex and non-linear constitutive property relations. Figure 4.3-1 illustrates this decomposition principle by showing how the overall model (a) is divided into two separate models by defining target property variables (b). These target variables are a set of solutions to both the formula balance model and the constitutive property design model. Each mathematical system is solved independent of the other until valid sets of solutions are found that satisfies both networks.


Conventional Model Structure

Decoupled Model Structure

(a)

(b)

Figure 4.3-1 Decoupling of Constitutive Equations for Reverse Problem Formulation.

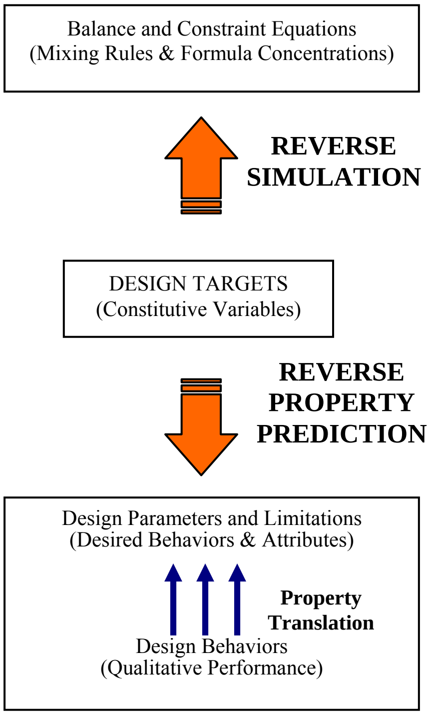


Figure 4.3-2 Decoupling of Case Study Model for Reverse Simulation.

Before an optimal process solution can be determined, the system must be decomposed into separate parts in order to reduce the complexity of finding simultaneous solutions. These subparts are comprised of formula equations, design parameters, and target property values.

Identification of an optimized formulation that is suitable for this entire decontamination system requires integration of all the interlacing characteristics of the coating composition that affect the film behavior. In order to accomplish this, an accurate representation of the system must be developed in order to solve the design parameters in terms of properties only. The representation of the design parameters along with the interactions between them and the overall formula behavior is given in Figure 4.3-3. This model could be solved as a reverse simulation using the final coating characteristics as input variables and the final polymer, solvent, and additive selections established as output solutions. The intricacy here is producing an accurate model, as the inherent non-linearity of the property relationships in conjunction with the complex formulation balance equations makes acquiring viable solutions difficult. In order to overcome these obstacles, the process of model decomposition is employed.

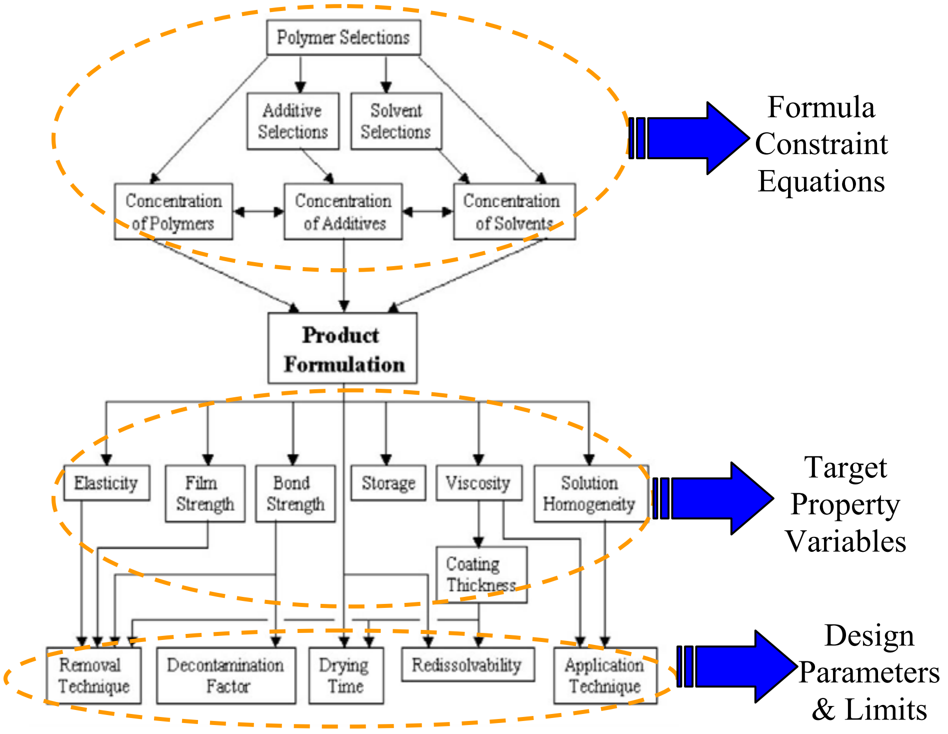


Figure 4.3-3 Schematic for Polymer Film Design & Model Decomposition.

The formula balance equations are separated into a reverse simulation that includes polymer, additive and solvent choices. Among these selections are available synthesis variables that affect polymeric properties such as molecular weight and extent of hydrolysis. With this information included in the model, not only can different polymer chains be compared, but also different variations of the same polymer and polymer blends. The ability to optimize the polymer synthesis as well as the film composition increases the possible formula combinations and improves the chances of acquiring an acceptable optimized formula. The additive options include components that enhance the desired film properties in order to fulfill the necessary constraints from the target property variables. This assortment of compounds contains wetting agents, surface tension reducers, biocides, cross-linking agents, elastomers, resin hardeners, dyes, pigments and dispersants. The choice of solvents is limited not only by the polymer selection, but also by the application. The list and amounts of volatile solvents allowed to be used on a nuclear power plant floor is extremely limited. The initial concentration of solvent present in the coating is the primary driving force involved with drying time. It is imperative for this part of the overall model to simultaneously optimize the formulation so that target properties are exhibited and the overall film behavior is superior to current competitor products.

The design parameters and limitations represent a compilation of attributes that the final product must exhibit. Because this formulation is intended to fulfill a market niche that already exists, the final formula characteristics are well known. The primary design parameters are the decontamination ability, drying time and redissolvability. The ability for the film to remove contaminates is measured by the ratio of radiation detected divided by the radiation present before the film removal. This numeric value is known as the decontamination factor and is a major selling point that must be equivalent or better than other possible decontamination products and processes. Another parameter where the new formulation must out perform the competing processes is drying time. Nuclear power plant outages are very costly and the schedule is optimized to minimize profit losses. By producing an optimized formula with the customer's major objectives in mind increases the marketability of the product and improves possible sales. The issue of redissolvability mostly pertains to the manner in which the film is disposed of. The current operations in nuclear plants involve the use of many different polymer based products that are sent to processing stations for redissolving and filtering. It is desired that the film can be disposed of by utilizing these same processing procedures. Other constraints include a simple and effective means to apply the coating to the walls and surfaces inside the plant as well as removal techniques. The model's main objective is to determine what intrinsic properties govern the desired performance variables and develop a dynamic set of target properties.

The development of a set of target properties allows this model to utilize reverse property prediction to identify the design alternatives. This is accomplished thru experimentation to determine what property ranges equate to final film behavior. In order to illustrate this modeling technique, we can simplify the system by assuming that the only major target property in Figure 4.3-3 is viscosity, which is the primary design constraints of the system because it's influences on many of the optimized coating behaviors including application technique, tensile and tear strength, film thickness, and redissolvablility. This simplified model is decoupled into two separate systems, the chemical makeup equations that produce a given viscosity and the behavioral models, which predict how the viscosity affects the design parameters and limitations.

The analysis of experimental data from formula variation tests produces a set of mixing rules for the system. When graphing this empirical model on over the two major component concentrations, polymer and elastomer, the resulting surface is illustrated in Figure 4.3-4(a), where any one point relates to a formula mixture.

By conducting laboratory tests and models to quantify the qualitative design behaviors, the optimum fluid viscosity that produces an adequate application behavior can be determined to be a given value, 1200 centipoise for example. This value becomes the viscosity design target of the qualitative prediction model. Once this is established, a surface plane is introduced at the design viscosity and creates a cross section of the viscosity surface. This cross section results in a constant property function chart that links polymer concentration to elastomer concentration. By developing this constant viscosity behavior curve, the ratios of the proper amount of solvent and additives to be incorporated for different polymer grades and blends to produce the desired property. This process is shown in Figure 4.3-4(b). These techniques seem unnecessary when considering only one target property, but when numerous targets are set, these simplification processes are extremely advantageous.

4.3.3 Results from the Optimization Techniques.

The ultimate result of this model aided in the development of a product that increases the removal rate of radioactive contaminates by 69% while attaining a 33% reduction in drying time over the current marketed competitors. The finalized product formula will be available through the Orex Technologies Catalog in Fall of 2005.

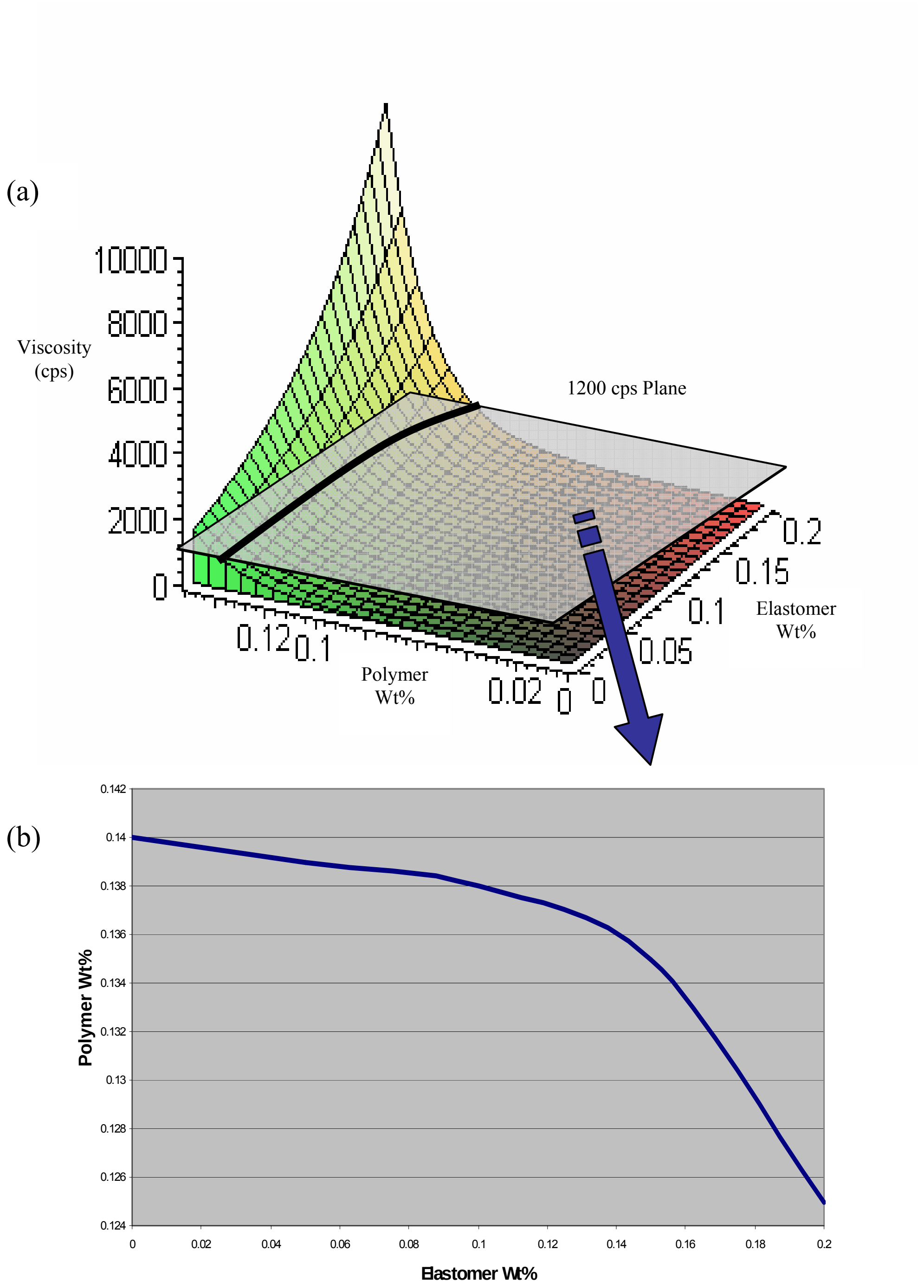


Figure 4.3-4 Formulation of Determining the Constant

Figure 4.3-5 Carbon Particle (50 mesh) Encapsulated in the Optimized Polymer Film Formula.

4.3.4 Conclusion.

By employing novel model development techniques such as property integration and model decomposition; a complex product formulation development process to determine “cradle to grave” optimized behavior has been simplified. In this work, these methods illustrated how engineering model development and optimization techniques must be modified and applied to industrial problems. This is presented to illustrate to students how creativity and a fundamental understanding of chemistry, engineering, and modeling can improve industrial ideas and practices.

4.4 Case Study III. Process Optimization Evaluation for Wastewater Treatment and/or Process Modifications to Reduce Contaminant Concentrations and Fulfill Government Regulations.

ETI(Eastern Technologies, Incorporated) is the sister company of Orex Technologies from Case Study II. They manage and process the discarded nuclear products created and manufactured by Orex. After the product's use and removal from the power plant, the polymer based merchandise containing the radioactive isotopes are sent to an ETI facility and is chemically treated and dissolved in a solvent processor, where separation of the radioactive metallic particles occurs. This process is illustrated in the following figure.

Figure 4.4-1(a) shows the contaminated materials being collected and prepared for processing. Once this is complete, the materials are loaded into batch reactors where the polymeric materials are treated. (Figure 4.4-1(b)) This stage is followed by a filtration step which can be seen in Figure 4.4-1(c) where only the collection of material to be disposed of as nuclear waste remains. Comparison of Figures 4.4-1(a) and 4.4-1(c) illustrate the dramatic volume reduction in waste material that makes these products and services so successful. In order for this novel technological service niche to remain possible, the material must be able to be disposed of easily and cost effectively, which is the driving force in this investigation. The popularity and success of the new Orex products and ETI processing service has caused the companies to grow at an alarming rate. The process is operating at near full capacity and the production rates are hindered by the state regulations governing the concentration of biological oxygen demand (BOD) allowable in their discharged wastewater stream.

Figure 4.4-1 ETI Processing Steps of Contaminated Radioactive Material.

The direct discharging of the filtered PVA solution from the solvent processor is not plausible, even though there is no associated toxicity with the compound. The unaltered PVA in the waste solution will develop a “skin” formation at the liquid-air interface surface of the discharge body of water without immediate dilution. The PVA in the waste stream must be subjected to some form of chemical degradation or breaking of the polymeric matrix to insure that the “skin” does not form and create an environmental hazard. As the polymer chains in the solution are broken, the solution’s viscosity decreases, improving the filterability, pumpability and process efficiency. However, this treatment creates large concentrations of organic acids and intermediate compounds as the polymer is broken apart piece by piece. These compounds cause the waste solution to have a high BOD, which is a measurement that determines a discharged waste stream’s possible impact on the ecosystem of the discharge body of water. Wastewater streams with excessively high BOD’s are not allowed to be discharged and permitting will be denied by the city and/or state.

4.4.1 Process Research & Development Methodology.

The dramatic increase in the use of the Orex products has created a greater demand on the processing equipment of ETI. The process is not taxed by long processing time constraints or management of loading and filtering the materials. The rate of disposal is limited by the release of BOD. More reactors could be constructed; however, they would not increase processing capacity because the liquid generated by the new process train could not be dumped due to regulation limits. The first and most obvious way to achieve a lower concentration of BODs in a single batch and increase the overall capacity by allowing more batches to be processed is to design and develop a waste water treatment process to reduce effluent concentrations. The standard wastewater treatment for BOD is either aerobic or anaerobic digestion. These treatment processes are very common and can be found at any municipal wastewater treatment facility around the globe. However, because the main objective of the project with ETI is to reduce waste, and in order to avoid creating large amounts of microbial yield and a new contaminated environmental hazard, this investigation emphasized anaerobic digestion, which is characterized by low microbial yields and will produce very little waste products. A bench scale water treatment process required to reduce the BOD concentration was constructed and evaluated. Figure 4.4-2 illustrates this process by providing the BOD removal rate at varying concentrations of PVA contaminate substrate concentrations. It can be seen that high concentrations of substrate inhibit the reaction kinetics. Because initial BOD concentration are between 2000 and 2500 mg/L, the rate of removal of contaminate in this system is very slow.

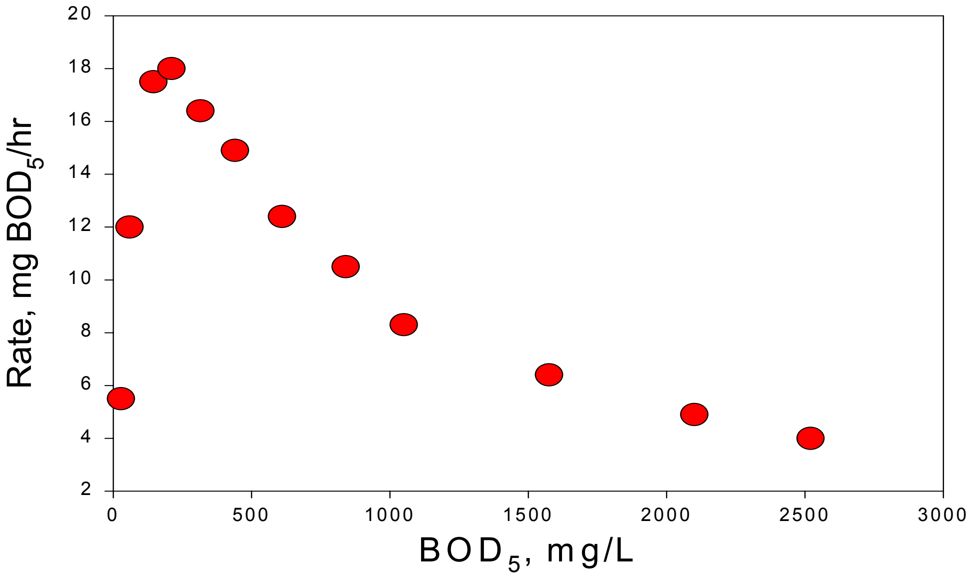


FIGURE 4.4-2 BOD Removal Rate of PVA Oxidized Constituents by Anaerobic Digestion.

With the proper kinetic model structure and process behaviors explained, it is possible to develop wastewater treatment simulations to aid in determining wastewater equipment configurations, sizes and multiple tank systems in order to maximize the rate removal in order to improve the system economics. Figure 4.4-3 demonstrates the dynamic substrate concentration in a batch-wise treatment scenario. The effluent BOD concentration take no less than 130 hours to decrease to acceptable values and are very slow because it is controlled by the rate limiting kinetics. This translates into extremely large and costly tanks ranging in size between 1 million and 2 million gallon capacities.

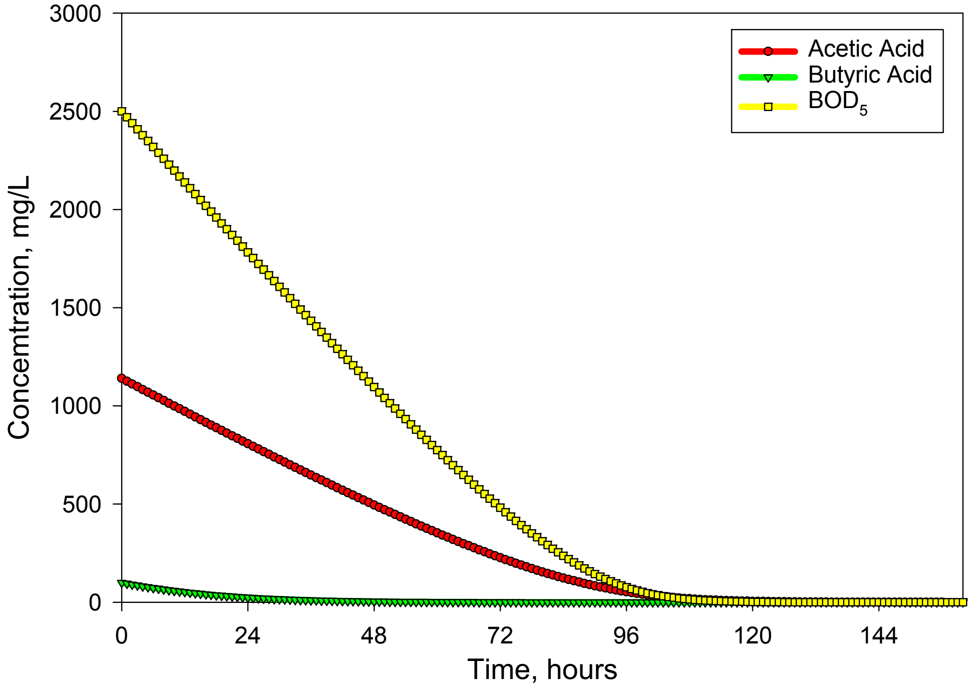


Figure 4.4-3 BOD Concentrations in a Batch Treatment Reactor for Oxidized PVA Constituents for Anaerobic Digestion.

Due to the waste water volume of the plant-wide operations, the use of batch water treatment facilities to remove water-soluble polymer constituents from wastewater streams will be limited, even though it achieves the best overall BOD removal. The more logistical wastewater treatment facility configuration consists of a series of smaller continuous feed stirred tank reactors with an overall resonance time of approximately 200 hours. The design of the system to operate at different optimum bulk concentrations will reduce the effective resonance time; however, this system will have to use complicated batch-wise start-up procedures. The method of "cradle to grave" optimization was employed to identify other options by evaluating the operations of the entire process.

4.4.2 Process Optimization & Modification Results.

By using the "cradle to grave" theory and optimizing the process parameters and disposal wastewater treatment simultaneously, like shown in Figure 4.4-1(b), the entire system produces acceptable product stream behaviors, maximum manufacturing profitability and efficiency, and minimum waste impacts and costs. Slight changes in the processing steps and equipment design parameters can drastically change the effluent BOD concentration and can reduce wastewater treatment time, size and cost. Many different aspects of the process were evaluated including the temperature of reaction, temperature and rate of addition of reactants, reactor heating and cooling, reactor mixing, reaction duration times and reaction extents. These process attributes had little effect on the overall process outcomes, but contributed to far-reaching variations in effluent BOD concentrations. These deviations are illustrated in Table 4.4-1.

Table 4.4-1 BOD Constituents in Sample Effluent Streams.

Sample	Vinyl Acetate	Formic Acid	Acetic Acid	Propionic Acid	Butyric Acid	Valeric Acid
I	0	7.9	478	15	108.6	4.9
II	0	0	418	12.7	131.7	0
III	0	5.2	45.2	0	4.4	0
IV	0	6.1	25.8	0	5.1	0
V	0	9	118.9	0	36.8	0
VI	8.5	9.2	22.3	12.1	87.7	0
VII	12.4	5.4	25.1	0	118.2	4.8

*Values are reported in ppm.

4.4.3 Conclusion.

By utilizing engineering fundamentals, non-linear analytical computer software, and creative chemistry, this processes system can be optimized to produce a reduced waste concentration stream and still provide the required processing tasks. All of the sample runs in Table 4.4-1 represent a single change made to a reactor configuration or parameter. The primary compound concentrations that make up the BOD in the solution are given for each process modification. With this information, a computer simulation model is developed and analyzed in conjunction with the process duties and designed outcomes in a “cradle to grave” optimization process. What is found from this very elementary analysis is an entire process that achieves the entire project goals with a BOD concentration 1/3 less than the previous operating value, which is 1/3 less than the allowable governmental discharge regulation limit. These process changes effectively increased the process capacity of the entire processing plant by 300% with less than 1% of the financial investment cost of the industry recommended water treatment system. This project stands out as an example of how creative problem solving, engineering know how and out of the box thinking can save millions of dollars on the plant floor.

4.5 Academic Consulting Impacts on Education—A Synopsis.

Because one of the most difficult challenges in technology-based curricula is familiarizing students with occupational environments and tasks, methods of identifying, analyzing, presenting, and familiarizing students with real world examples must be instituted. The creative use of the academic concepts and theory in advancements addressing current industrial needs through academic consulting programs are one of these new successful techniques. As the technological knowledge of mankind advances, the division between the fundamental executions of thought and advanced theoretical academic research increases beyond the point where presentation of creative investigative techniques in the classroom found in the laboratory cannot be presented due to the complexity of the research project. Because of this ever increasing gap, special programs around the world have been developed in order to regain a comprehensive view of engineering fundamentals in undergraduate programs that focus on current trends, issues and direction in the methods, ideology, and technologies used by today's industrial leaders and better prepare the student to enter the technological workforce.

This work specifically addresses the growing concern of the associated costs of waste contamination, removal and governmental regulation compliance in manufacturing industries. The new process and product optimization technique of "cradle to grave" analysis was developed, implemented, and illustrated to promote the creative nature of student thinking and fundamental application in complicated technological systems. This work is presented to encourage the integration of more creative applications of academic theories with real world industrial problem solving in science, math, engineering and technology education.

4.6 Acknowledgements.

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APPENDICES

Appendix A: STRIPPABLE PVA COATINGS AND METHODS OF MAKING AND USING THE SAME.

STRIPPABLE PVA COATINGS AND METHODS OF MAKING AND USING THE SAME.

This patent application claims the benefit of priority to U.S. Provisional Patent Application Serial No. 60/505,179 entitled "STRIPPABLE PVA COATINGS AND METHODS OF MAKING AND USING THE SAME" filed on September 23, 2003, the subject matter of which is incorporated herein in its entirety.

Field of the Invention.

The present invention relates to strippable polyvinyl alcohol (PVA) coatings for use in industry. The present invention further relates to methods of making and using strippable polyvinyl alcohol (PVA) coatings.

Background of the Invention.

There exists a need in the art for effective methods and products for detecting, handling, removing, and minimizing radioactive waste and contaminants in the nuclear industry.

Summary of the Invention.

The present invention is directed to strippable polyvinyl alcohol (PVA) coatings. The present invention is further directed to methods of making and using the strippable polyvinyl alcohol (PVA) coatings. In one exemplary method, the strippable polyvinyl alcohol (PVA) coatings are applied to a surface, removed from the surface after a desired period of time, and then disposed of by solubilizing the water-soluble material of the strippable polyvinyl alcohol (PVA) coatings.

The present invention is also directed to methods of removing one or more contaminants from an object, wherein the method comprises applying a strippable polyvinyl alcohol (PVA) coating onto the product, and removing the strippable polyvinyl alcohol (PVA) coating from the object after a desired period of time.

These and other features and advantages of the present invention will become apparent after a review of the following detailed description of the disclosed embodiments and the appended claims.

Detailed Description of the Invention.

To promote an understanding of the principles of the present invention, descriptions of specific embodiments of the invention follow and specific language is used to describe the specific embodiments. It will nevertheless be understood that no limitation of the scope of the invention is intended by the use of specific language. Alterations, further modifications, and such further applications of the principles of the present invention discussed are contemplated as would normally occur to one ordinarily skilled in the art to which the invention pertains.

The present invention involves the use of a polyvinyl alcohol (PVA) matrix that is applied to surfaces as part of a decontamination system. The PVA coating serves to initially “fix” the contaminants in place for contaminant detection and ultimate removal. The PVA coating not only functions to mechanically entrap radioactive contaminants, but also contains one or more compounds that selectively entrap or bind certain radioactive isotopes or species to the PVA matrix. After use, the PVA coating containing one or more contaminants may be disposed of by dissolving the PVA coating and, if necessary, such as in the case of radioactive contaminants, separating the one or more contaminants from the dissolved PVA.

The PVA coatings of the present invention are described in detail below.

PVA Coating Composition.

The PVA coatings of the present invention may comprise one or more of the following components:

PVA .

The PVA coatings of the present invention contain at least one PVA. Suitable PVAs for use in the present invention desirably have the following properties: (1) water solubility in water having a water temperature of at least about 20°C, and (2) enables a coating made therefrom to remain stable at room temperature. The PVA may be designed to have a water solubility ranging from about 20°C to about 90°C. For example, the PVA may be soluble in water having a water temperature of at least about 20°C, or at least about 37°C, or at least about 50°C, or at least about 75°C, or at least about 90°C.

The one or more PVAs may be present in an amount of up to about 50 wt% or higher based on a total weight of the PVA coating. Desirably, the one or more PVAs are present in an amount ranging from about 5.0 to about 50.0 wt% based on a total weight of the PVA coating. More desirably, the one or more PVAs are present in an amount ranging from about 5.0 to about 25.0 wt% based on a total weight of the PVA coating.

A number of commercially available PVAs may be used in the present invention. Suitable commercially available PVAs include, but are not limited to, PVAs commercially available under the trade designation EVANOL® from E. I. DuPont & Company (Wilmington, DE). In one desired embodiment of the present invention, the PVA comprises EVANOL® 90-50 from E. I. DuPont & Company. In another desired embodiment of the present invention, the PVA comprises EVANOL® 71-30 from E.I. DuPont & Company.

Glycerol .

The PVA coatings of the present invention desirably contain glycerol. Glycerol provides elasticity to the PVA coatings of the present invention.

The glycerol may be present in an amount of up to about 10.0 wt% based on a total weight of the PVA coating. Desirably, the glycerol is present in an amount ranging from about 2.0 to about 10.0 wt% based on a total weight of the PVA coating. More desirably, the glycerol is present in an amount ranging from about 4.0 to about 8.0 wt% based on a total weight of the PVA coating.

A number of commercially available glycerols may be used in the present invention. Suitable commercially available glycerols include, but are not limited to, glycerols commercially available from Lonza, Inc. (Fairlawn, NJ) and Equistar (Dallas, TX).

Chelating/Complexing Agents.

The PVA coatings of the present invention desirably contain one or more chelating and/or complexing agents. The chelating and/or complexing agents may be added to the PVA matrix of the PVA coating to target specific radioactive metals, such as to target Fe (iron), Mg (magnesium), Mn (manganese) and/or Co (cobalt). The added chelating and/or complexing agents may be added to the PVA coatings to enhance binding of the radioactive target metals. Modifications may be made to the chelating/complexing agents to make them more soluble, to bind them chemically to the PVA matrix, and/or to attach molecules with fluorescent labels.

A variety of chelating and/or complexing agents may be used in the present invention as described below.

Chelating Compounds/Polymers.

The PVA coatings of the present invention may include one or more chelating agents. Such chelating agents are particularly useful to target the removal of radioactive cobalt. Suitable chelating agents include, but are not limited to, ethylenediamine-tetraacetic acid (EDTA); a chelating copolymer having a hydrophobic backbone and hydrophilic side groups attached thereto, wherein the hydrophilic side groups comprise essentially half of an EDTA molecule such as in the exemplary formula as shown below:

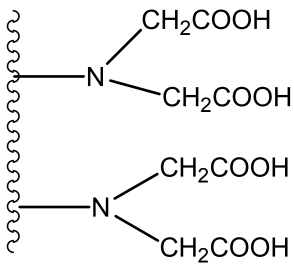


Figure 1 Polymer Chain Configuration.

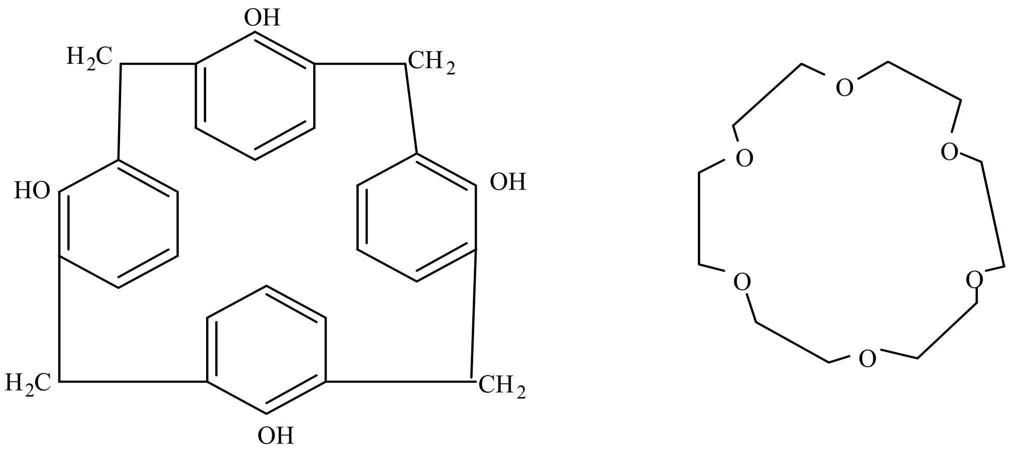
wherein 〰〰〰 represents the copolymer chain; or a mixture thereof. Suitable chelating copolymers include, but are not limited to, copolymers having a polymer chain formed from styrene and divinylbenzene monomers.

The above-described copolymers have a high selectivity of transition metal ions like Co+2 and Co+3 even in high salt concentrations.

In one desired embodiment of the present invention, the PVA coatings include EDTA alone or in combination with one or more additional chelating and/or complexing agents described herein. When present, EDTA is desirably present in the PVA coatings of the present invention in an amount of up to about 5 wt% based on a total weight of the PVA coating. More desirably, the EDTA is present in an amount ranging from greater than 0 to about 1.0 wt% based on a total weight of the PVA coating.

Arene or Crown Ether Compounds.

The PVA coatings of the present invention may also include one or more arene and/or crown compounds. Arene and/or crown compounds have high selectivity for extraction of cesium (Cs) from contaminated surfaces. Suitable arene and/or crown compounds include, but not limited to, calix-4-arene and 18-crown-6 ether shown below.



Calix-4-arene

18-crown-6

Figure 2 ***Arene and Crown Ether Compounds.***

In one desired embodiment of the present invention, the above-referenced complexing agents are present in the PVA coating at a ratio of two 18-crown-6 molecules per molecule of calix-4-arene. Suitable initial concentrations of the complexing agents may be 0.007 M of calix-4-arene and 0.014 M 18-crown-6.

Since the PVA emulsions of the present invention have a high water content, it is believed that the Cs on a contaminated surface of an object migrates into the PVA and is bound by the calix-4-arene and/or 18-crown-6 compounds.

Water solubility of the calix-4-arene may be improved by the addition of sulfonated groups on the aryl rings as disclosed in the methods of Mathieu et al. (See, Mathieu et al., Water-soluble para-sulfonated 1,2,3,4-calix-4-arene bis crowns in the cone configuration, Tetrahedron Letters (2002), 43, 1225-1229.)

When any of the above-described chelating/complexing agents are present in the PVA coatings of the present invention, each chelating/complexing agent is desirably independently present in the PVA coatings in an amount of up to about 5 wt% based on a total weight of the PVA coating. More desirably, each chelating and/or complexing agent is independently present in an amount ranging from greater than 0 to about 1.0 wt% based on a total weight of the PVA coating.

Surfactants.

The PVA coatings of the present invention may comprise one or more surfactants. Suitable surfactants for use in the present invention provide one or more of the following features: (1) acts as a dispersant to evenly disperse PVA polymers, metal particles, chelating/complexing agents (when present), other components, or a combination thereof; (2) acts to increase the efficiency of the coating in removing contaminants; (3) acts to improve the shelf life of unused PVA coating solutions; and (4) acts to reduce the surface tension of the coating composition. Suitable surfactants for use in the present invention include, but are not limited to, sodium polynaphthalene sulfonate surfactants, polyether modified polydimethyl-siloxane surfactants, nonionic ethoxylated alcohols having from about 6 to about 10 ethylene oxide units per molecule, and combinations thereof. Desirably, the PVA coatings of the present invention comprise one or more nonionic surfactants including, but are not limited to, nonionic ethoxylated alcohols having from about 6 to about 10 ethylene oxide units per molecule.

The one or more surfactants may be present in the PVA coatings of the present invention an amount of up to about 5.0 wt% based on a total weight of the PVA coating. Desirably, the one or more surfactants are each independently present in an amount ranging from about greater than 0 to about 1.0 wt% based on a total weight of the PVA coating.

A number of commercially available surfactants may be used in the present invention. Suitable commercially available surfactants include, but are not limited to, sodium polynaphthalene sulfonate surfactants available under the trade designation REACT-RITE® Dispersant #1; polyether modified polydimethyl-siloxane surfactants available from BYK-Chemie USA Inc. (Wallingford, CT) under the trade designation BYK-348; and nonionic ethoxylated alcohol surfactants sold under the trade designation TRITON™, available from Union Carbide Corporation (South Charleston, WV), such as TRITON™ X100 (t-octylphenoxypolyethoxyethanol) (a nonionic ethoxylated alcohols having 9.5 ethylene oxide units per molecule).

In one desired embodiment of the present invention, the PVA coating comprises REACT-RITE® Dispersant #1 in an amount of greater than 0 to about 1.0 wt% based on a total weight of the PVA coating, and BYK-348 in an amount of greater than 0 to about 1.0 wt% based on a total weight of the PVA coating.

Solvent Systems.

The PVA coatings of the present invention comprise water as a primary solvent or carrier, but may also include other solvents in combination with water as described below.

Water.

Soft or hard water may be used in the present invention, although soft water is more desirable. As used herein, the term "soft water" refers to water containing less than about 60 ppm of calcium carbonate. As used herein, the term "hard water" refers to water containing more than about 60 ppm of calcium carbonate, while "very hard water" refers to water containing more than about 180 ppm of calcium carbonate. The PVA coatings of the present invention may be formed using water available from any source, including any municipal water-treatment facility.

The PVA coatings of the present invention typically comprise up to about 90 weight-percent (wt%) of water based on a total weight of the PVA coating. Desirably, the PVA coatings of the present invention comprise from about 30 to about 85 wt% water based on a total weight of the PVA coating. More desirably, the PVA coatings of the present invention comprise from about 50 to about 80 wt% water based on a total weight of the PVA coating.

Ethanol.

Ethanol may also be used in combination with water to form a suitable solvent system for the PVA coatings of the present invention. Desirably, the ethanol is denatured ethanol. The ethanol assists in the curing rate and evaporation rate of the applied PVA coating, improving the curing time and speed of the entire decontamination process.

When present, the ethanol may be present in the PVA coatings of the present invention an amount of up to about 25.0 wt% based on a total weight of the PVA coating. Desirably, the ethanol is present in an amount ranging from about greater than 0 to about 15.0 wt% based on a total weight of the PVA coating.

Additives.

The PVA coatings of the present invention may further comprise one or more of the following additives.

Colorants.

The PVA coatings of the present invention may also comprise one or more colorants to assist in the identification of applied PVA coatings on various surfaces. Further, in some embodiments, the colorants may exhibit a color change, which indicates the presence of radioactive material within the PVA coating. In one embodiment, a yellow, red or orange colorant is added to a PVA coating.

The one or more colorants may be present in the PVA coatings of the present invention an amount of up to about 6.0 wt% based on a total weight of the PVA coating. Desirably, the one or more colorants are present in an amount ranging from about greater than 0 to about 5.0 wt% based on a total weight of the PVA coating.

pH Control Agents.

The PVA coatings of the present invention may also comprise one or more components to adjust/control the pH of the PVA coating. Desirably, the PVA coating has a pH in the range of from about 1 to about 12, more desirably, from about 3 to about 10. Typically, when present, the one or more pH control agents are present in an amount of up to about 10 wt% based on a total weight of the PVA coating in order to obtain a desired pH for the PVA coatings.

Suitable pH control agents include, but are not limited to, inorganic acidic compounds including sodium hydrogen sulfate, calcium phosphate and hydrogen phosphate; organic acid compounds including carboxylic acids such as oxalic acid, and polyacrylic acid; inorganic alkaline compounds including hydroxides, silicates, and carbonates; and organic alkaline compounds including amines and alkoxides.

Fiber Reinforcements.

The PVA coatings of the present invention may further comprise water-soluble fibers, such as PVA fibers. Suitable PVA fibers and methods of making PVA fibers are disclosed in U.S. Patents Nos. 5,181,967; 5,207,837; 5,268,222; 5,620,786; 5,885,907; and 5,891,812; the disclosures of all of which are hereby incorporated in their entirety by reference. An example of a suitable polyvinyl alcohol fiber for use in the present invention is a polyvinyl alcohol homopolymer that has been highly crystallized by post-drawing or by heat annealing.

The water-soluble fibers may be present in the PVA coatings of the present invention as individual fibers, such as chopped PVA fibers, having an average fiber length of less than about 2.54 cm (1 inch).

When present, the water-soluble fibers may be present in the PVA coatings of the present invention an amount of up to about 25.0 wt% based on a total weight of the PVA coating. Desirably, the water-soluble fibers, when present, are present in an amount ranging from about greater than 0 to about 15.0 wt% based on a total weight of the PVA coating.

Biocides.

The PVA coatings of the present invention may also comprise one or more biocides to prevent the growth of organisms in the PVA coating materials and/or the PVA coating. The one or more biocides may be present in the PVA coatings of the present invention an amount of up to about 5.0 wt% based on a total weight of the PVA coating.

Desirably, the one or more biocides are present in an amount ranging from about greater than 0 to about 1.0 wt% based on a total weight of the PVA coating.

Suitable biocides for use in the present invention include, but are not limited to, triclosan and other antimicrobial agents commercially available under the trade designation MICROBAN®; and antimicrobial agents sold under the trade designation DOWICIL™, available from Dow Chemical Company (Midland, MI), such as DOWICIL™ 75 (active ingredient: 1-(3-chloroallyl)-3,5,7-triaza-1-azoniaadamantane chloride).

Methods of Making The PVA Coating Compositions.

The PVA coatings of the present invention may be prepared using conventional mixing techniques. The components for forming the PVA coatings may be combined with water in any order at room temperature. Typically, PVA coatings are prepared by combining the components in the following order while mixing: water, one or more additional solvents (when present), one or more surfactants (when present), PVA, glycerol, one or more chelating/complexing agents (when present), one or more pH control agents (when present), and one or more additives (when present).

Methods of Using The PVA Coating Compositions.

The strippable PVA coatings of the present invention have significant advantages over traditional coatings. The strippable PVA coatings of the present invention may possess additional components to improve decontamination effectiveness via chemical bonding with subject contamination. The PVA-based coating offers distinct advantages, most notably the ability to volume-reduce efficiently the subsequent waste created during a decontamination operation. PVA formulations may be made readily solubilizable, oxidizable and break down to a relatively benign form following use. The present invention offers a unique “cradle-to-grave” approach that provides significant waste management benefits.

The strippable PVA coatings may be used in both the commercial and government nuclear industries. Strippable coatings of the present invention have a number of advantages over other popular decontamination methods. A strippable PVA coating can be applied to a surface quickly, thus “fixing” the contaminants in place and mitigating further spread and additional contact or uptake by personnel. Depending on contamination levels and associated dose rates involved, access and/or work in the area may continue at a substantially reduced exposure risk once the contaminants are fixed to the surfaces involved. The strippable PVA coatings can subsequently be removed or “stripped” from the surfaces, removing the contaminants with the coating. The contaminated coatings are then packaged and transported, if necessary, for final disposition. There are no liquid waste streams associated with the use of these coatings thus eliminating the burden of managing large volumes of liquid radioactive wastes that sometimes accompany other popular decontamination methods.

The stripped PVA coatings latent with captured radionuclides desirably do not contain species listed by RCRA, CWA and SARA (e.g. EPA’s List of List) and other environmental regulations and thereby complicate its subsequent disposition.

The PVA coatings of the present invention may be applied to a variety of substrates, such as rough substrates (e.g. concrete) and smooth substrates (e.g. marble).

Such substrates have wide variations in composition and bonding affinities for potential contaminants. The PVA coatings may be applied using any conventional application including, but not limited to, brushing, spraying, etc.

In one desired embodiment of the present invention, the PVA coating is used to remove one or more radioactive contaminants from a surface. The method of removing one or more radioactive contaminants from a surface of an object may comprise the steps of (1) applying a strippable film to the surface of the object, wherein the strippable film comprises polyvinyl alcohol (PVA), water, and at least one surfactant; and (2) removing the strippable film from the surface of the object.

Methods of Disposing of Stripped PVA Coatings.

The present invention is further directed to methods of disposing of the stripped PVA coatings. The method of disposing of the stripped PVA coatings is desirably one of the methods disclosed in U.S. Patent No. 6,623,643, filed on September 23, 2003; International Publication No. WO 01/36338 corresponding to PCT Application No. PCT/US00/26553; and PCT Application No. PCT/US02/16184, filed on May 22, 2002; the disclosures of all of which are hereby incorporated in their entirety by reference. In these methods of disposal, the method may include one or more of the following steps:

(1) placing the stripped PVA coating into a disposal reactor;

(2) introducing water into the reactor to form a solution;

(3) optionally introducing a pH adjusting agent, such as an acid (e.g., acetic acid) or a base (e.g., sodium hydroxide), to the solution;

(4) adding a degradation-enhancing reactant or a precursor of a degradation-enhancing reactant to the solution;

(5) heating the aqueous solution so as to react the precursor to form the degradation-enhancing reactant, if necessary, and reacting with the water-soluble polymer of the stripped PVA coating to form one or more degradation products;

(6) optionally, filtering non-solubilized material from the aqueous environment;

(7) optionally, measuring a parameter indicator of the concentration of polymer material in the aqueous environment;

(8) optionally, filtering material, e.g., radioactive material, from the aqueous environment;

(9) optionally, altering, e.g., neutralizing, the pH of the aqueous environment;

(10) optionally, biodegrading the resulting degradation products in the aqueous environment, e.g., organic acids form CO2, H2O and biomass; and

(11) removing any insoluble components from the reactor.

While the specification has been described in detail with respect to specific embodiments thereof, it will be appreciated that those skilled in the art, upon attaining an understanding of the foregoing, may readily conceive of alterations to, variations of, and equivalents to these embodiments. Accordingly, the scope of the present invention should be assessed as that of the appended claims and any equivalents thereto.

What is Claimed is:

1. A strippable film composition comprising polyvinyl alcohol (PVA), water and at least one surfactant.

2. The strippable film composition of Claim 1, wherein the at least one surfactant comprises a sodium polynaphthalene sulfonate surfactant, a polyether modified polydimethyl-siloxane surfactant, a nonionic ethoxylated alcohol surfactant having from about 6 to about 10 ethylene oxide units per molecule, or a combination thereof.

3. The strippable film composition of Claim 2, wherein the composition comprises greater than 0 up to about 5.0 wt% of a nonionic ethoxylated alcohol surfactant having from about 6 to about 10 ethylene oxide units per molecule, based on a total weight of the strippable film composition.

4. The strippable film composition of Claim 1, further comprising glycerol in an amount of greater than 0 up to about 10.0 wt%, based on a total weight of the strippable film composition.

5. The strippable film composition of Claim 1, further comprising ethanol in an amount of greater than 0 up to about 15.0 wt%, based on a total weight of the strippable film composition.

6. The strippable film composition of Claim 1, further comprising at least one chelating agent in an amount of greater than 0 up to about 1.0 wt%, based on a total weight of the strippable film composition.

7. The strippable film composition of Claim 6, wherein the at least one chelating agent comprises ethylenediamine-tetraacetic acid (EDTA).

8. The strippable film composition of Claim 1, further comprising at least one colorant in an amount of greater than 0 up to about 5.0 wt%, based on a total weight of the strippable film composition.

9. The strippable film composition of Claim 1, further comprising at least one biocide in an amount of greater than 0 up to about 5.0 wt%, based on a total weight of the strippable film composition.

10. The strippable film composition of Claim 9, wherein the at least one biocide comprises 1-(3-chloroallyl)-3,5,7-triaza-1-azoniaadamantane chloride.

11. The strippable film composition of Claim 1, wherein the composition comprises:

from about 50 to about 90 wt% water;

from about 5.0 to about 20.0 wt% PVA;

up to about 5.0 wt% of a nonionic ethoxylated alcohol surfactant having from about 6 to about 10 ethylene oxide units per molecule;

from about 4.0 to about 10.0 wt% glycerol;

up to about 1.0 wt% EDTA;

up to about 5.0 wt% of at least one colorant; and

up to about 5.0 wt% of at least one biocide;

wherein all weight percentages are based on a total weight of the strippable film composition.

12. The strippable film composition of Claim 1, wherein the composition comprises:

from about 50 to about 90 wt% water;

from about 5.0 to about 20.0 wt% PVA;

up to about 5.0 wt% of a nonionic ethoxylated alcohol surfactant having about 9.5 ethylene oxide units per molecule;

from about 4.0 to about 10.0 wt% glycerol;

up to about 1.0 wt% EDTA;

up to about 5.0 wt% of at least one colorant; and

up to about 5.0 wt% of at least one biocide comprising 1-(3-chloroallyl)-3,5,7-triaza-1-azoniaadamantane chloride;

wherein all weight percentages are based on a total weight of the strippable film composition.

13. The strippable film composition of Claim 1, wherein the composition comprises:

from about 50 to about 90 wt% water;

from about 5.0 to about 20.0 wt% PVA;

from greater than 0 up to about 5.0 wt% of sodium polynaphthalene sulfonate, polyether modified polydimethyl-siloxane, a nonionic ethoxylated alcohol surfactant having from about 6 to about 10 ethylene oxide units per molecule, or a combination thereof;

from about 4.0 to about 10.0 wt% glycerol;

from greater than 0 up to about 1.0 wt% EDTA;

from greater than 0 up to about 5.0 wt% of at least one colorant; and

from greater than 0 up to about 5.0 wt% of at least one biocide;

wherein all weight percentages are based on a total weight of the strippable film composition.

14. The strippable film composition of Claim 1, further comprising at least one chelating or complexing agent selected from EDTA; a chelating copolymer having a hydrophobic backbone and hydrophilic side groups attached thereto, wherein the hydrophilic side groups comprise half of an EDTA molecule; crown ethers; calix-4-arene; and combinations thereof.

15. The strippable film composition of Claim 14, wherein the strippable film composition comprises 18-crown-6 ether.

16. The strippable film composition of Claim 14, wherein the strippable film composition comprises 18-crown-6 ether and calix-4-arene.

17. The strippable film composition of Claim 14, wherein the strippable film composition comprises a calix-4-arene having one or more sulfonate groups on one or more aryl rings of the calix-4-arene.

18. The strippable film composition of Claim 14, wherein the strippable film composition comprises a chelating copolymer of styrene and divinylbenzene.

19. A method of removing radioactive contaminants from a surface of an object, said method comprising the steps of:

applying a strippable film composition to the surface of the object, wherein the strippable film composition comprises polyvinyl alcohol (PVA), water and at least one surfactant; and

removing the strippable film composition from the surface of the object.

20. The method of Claim 19, wherein the at least one surfactant comprises a sodium polynaphthalene sulfonate surfactant, a polyether modified polydimethyl-siloxane surfactant, a nonionic ethoxylated alcohol surfactant having from about 6 to about 10 ethylene oxide units per molecule, or a combination thereof.

21. The method of Claim 20, wherein the composition comprises greater than 0 up to about 5.0 wt% of a nonionic ethoxylated alcohol surfactant having from about 6 to about 10 ethylene oxide units per molecule, based on a total weight of the strippable film composition.

22. The method of Claim 19, wherein the composition further comprises at least one biocide in an amount of greater than 0 up to about 5.0 wt%, based on a total weight of the strippable film composition.

23. The method of Claim 22, wherein the at least one biocide comprises 1-(3-chloroallyl)-3,5,7-triaza-1-azoniaadamantane chloride.

24. The method of Claim 19, wherein the composition comprises:

from about 50 to about 90 wt% water;

from about 5.0 to about 20.0 wt% PVA;

up to about 5.0 wt% of a nonionic ethoxylated alcohol surfactant having from about 6 to about 10 ethylene oxide units per molecule;

from about 4.0 to about 10.0 wt% glycerol;

up to about 1.0 wt% EDTA;

up to about 5.0 wt% of at least one colorant; and

up to about 5.0 wt% of at least one biocide;

wherein all weight percentages are based on a total weight of the strippable film composition.

25. The method of Claim 19, wherein the composition comprises:

from about 50 to about 90 wt% water;

from about 5.0 to about 20.0 wt% PVA;

from greater than 0 up to about 5.0 wt% of sodium polynaphthalene sulfonate, polyether modified polydimethyl-siloxane, a nonionic ethoxylated alcohol surfactant having from about 6 to about 10 ethylene oxide units per molecule, or a combination thereof;

from about 4.0 to about 10.0 wt% glycerol;

from greater than 0 up to about 1.0 wt% EDTA;

from greater than 0 up to about 5.0 wt% of at least one colorant; and

from greater than 0 up to about 5.0 wt% of at least one biocide;

wherein all weight percentages are based on a total weight of the strippable film composition.

26. The method of Claim 19, wherein the applying step comprises spraying the strippable film composition onto the surface of the object.

27. The method of Claim 19, wherein the applying step comprises brushing the strippable film composition onto the surface of the object.

28. The method of Claim 19, further comprising:

placing the strippable film composition into a disposal reactor;

introducing water into the reactor to form an aqueous solution;

heating the aqueous solution to dissolve or degrade the PVA of the strippable film composition; and

separating at least a portion of the radioactive contaminants from the PVA and the aqueous solution.

29. A strippable film composition consisting essentially of:

a single polymer, wherein the single polymer is polyvinyl alcohol (PVA);

water;

glycerol;

EDTA;

a nonionic ethoxylated alcohol surfactant having about 9.5 ethylene oxide units per molecule;

a biocide comprising 1-(3-chloroallyl)-3,5,7-triaza-1-azoniaadamantane chloride; and

at least one colorant.

STRIPPABLE PVA COATINGS AND METHODS OF MAKING AND USING THE SAME

ABSTRACT OF THE DISCLOSURE

Strippable polyvinyl alcohol (PVA) coatings and methods of making, using and disposing of strippable PVA coatings are disclosed.

Appendix B: OREX DECONTAMINATION FILM “MOLEX” MATERIAL AND SAFETY DATA SHEET.

OREX ADVANCED PROTECTIVE CLOTHING TECHNOLOGY

Material Safety Data Sheet

MoleX Decontamination Coating (Liquid State)

SECTION I - **Chemical Product and Company Identification**

Material Identificaiton: MoleX Decontamination Coating
Company Identification: Orex Technologies International
1850-E Beaver Ridge Circle
Norcross, GA 30071
Information Number: (903)624-9632
CHEMTREC Hotline: (800)424-9300

NFPA rating(estimated):
Health: **1**
Flammability:
Reactivity: **0**

SECTION II - **Composition, Information of Ingredients**

Components

Material	CAS Number	%
Vinyl Alcohol Polymers and Copolymers	9002-89-5	0-99
	25213-24-5	0-99
	54626-91-4	0-99
Glycerol	56-81-5	0-99
Water	7732-18-5	0-99
Process Aids	Proprietary	0-3
Polyethylene glycol P-1,1,3,3 -tetramethylbutylphenyl ether	9002-93-1	<2
Acrylic Resin	Proprietary	<2
Methanol	67-56-1	<0.5
Sodium Acetate	127-09-3	<0.5

SECTION III - **Hazards Identification**

Emergency Overview

Appearance:	Viscous Orange Liquid.
Target Organs:	None are known.
Chronic Effects:	None are known.
Medical Conditions Aggravated by Exposure:	None are known.
Carcinogenicity:	None
Eye:	May cause eye irritation.
Skin:	May cause skin irritation.
Ingestion:	Ingestion of large amounts may cause gastrointestinal irritation. Low hazard for usual industrial handling.
Inhalation:	Inhalation of a mist of this material may cause respiratory tract irritation. Low hazard for usual industrial handling.

SECTION IV - **First Aid Measures**

First Aid Instructions

Eyes:	Flush eyes with flowing water for at least 15 minutes, occasionally lifting the upper and lower eyelids. If irritation develops, consult a physician.
Skin:	Wash affected skin areas with soap and water. If irritation develops, consult a physician.
Ingestion:	If swallowed, dilute with water and induce vomiting. Never give anything by mouth to an unconscious person. Get immediate medical attention.
Inhalation:	Remove from exposure and move to fresh air immediately. If not breathing, give artifical respiration. If breathing is difficult, give oxygen. Consult a physician if cough or other symptoms persists.
Notes to Physician:	Treat symptomatically and supportively.

SECTION V - **Fire Fighting Measures**

Flammable Properties

Flash Point Temperature:	N/A
Autoignition Temperature:	N/A
Flammability Limits in Air:	N/A
Extinguishing Medium:	Use water, foam, dry chemical or extinguishing media proper to primary cause of fire.
Fire Fighting Instructions:	Wear a self-contained breathing apparatus in pressure demand, MSHA/NIOSH (approved or equivalent), and full protective gear.

Incomplete combustion, thermal degradation and hydrocarbon oxidation generate highly toxic gases including carbon monoxide, organic acids, aldehydes, alcohols, and oxides of sodium.

SECTION VI - **Accidental Release Measures**

Safeguards

Personnel-	Use proper personal protective equipment as indicated in Section VIII.
Spill/Leaks-	Absorb any spillage from floor areas. Rinse with soap and water to insure no residue will form to further avoid slipping hazards.

SECTION VII – **Handling and Storage**

Handling:	Wash thoroughly after handling. Wash hands before eating. Use with adequate ventilation. Avoid contact with eyes, skin, and clothing. Keep container tightly closed. Avoid ingestion and inhalation. Wash clothing before reuse.
Storage:	Store in a tightly closed container to prevent evaporation. Keep containers in a cool, dry, well ventilated area away from incompatible substances. No special precautions are indicated.

SECTION VIII – **Exposure Controls, Personal Protection**

Engineering Controls:

Facilities storing or utilizing this material should be equipped with an eyewash facility and safety shower. Use adequate ventilation to keep airborne concentrations low. In the event the liquid is heated above 200 C (392 F), local ventilation should be used to avoid exposure to fumes.

Exposure Guidelines:

Vinyl Alcohol Polymers and Copolymers
PEL (OSHA) N/A
TLV (ACGIH)N/A

Glycerol
PEL (OSHA) 15mg/m^3 TWA(total dust) / 5 mg/m^3 TWA(respirable fraction)
TLV (ACGIH)10 mg/m^3

Methanol
PEL (OSHA) 200ppm, 260mg/m^3, 8 hr. TWA
TLV (ACGIH)200ppm, 8 hr. TWA, Skin STEL 250ppm

Sodium Acetate
PEL (OSHA) N/A
TLV (ACGIH)N/A

Polyethylene glycol P-1,1,3,3-tetramethylbutylphenyl ether
ORL-RAT LD50 1800mg/kg
IVN-MUS LD50 375mg/kg

Personal Protective Equipment:

Eye/Face Protection- Wear safety glasses as described by OSHA's eye and face protection regulations in 29 CFR 1910.133 or European Standard EN166. Use coverall chemical splash goggles and face shield when possibility exists for eye and face contact due to splashing or spraying of molten material. A full-face mask respirator provides protection from eye contamination.

Respirators- Follow the OSHA respirator regulations found in 29 CFR 1910.134 or European Standard EN149. A NIOSH/MSHA approved air purifying respirator with an organic vapor cartridge with a dust/mist filter may be permissible under certain circumstances where airborne concentrations are expected to exceed exposure limits. Protection provided by air purifying respirators is limited. Use a positive pressure air supplied respirator if there is any potential for an uncontrolled release, exposure levels are not known, or any other circumstances where air purifying respirators may not provide adequate protection.

Protective Clothing- Wear appropriate protective gloves and clothing to minimize skin exposure.

SECTION IX – **Physical and Chemical Properties**

Physical Data

Appearance:	Viscous Orange Liquid
Odor:	Faint Odor
Boiling Point:	90-100 degrees Centigrade
Freezing Point:	5 degrees Centigrade
Melting Point (polymer):	200 degrees Centigrade
Solubility:	Dispersible in Water; Insoluble in Chloroform
Physical State:	Liquid
Specific Gravity/Bulk Density:	1.13
Viscosity:	>3500cps.
pH:	6-8.5

SECTION X – **Stability and Reactivity**

Chemical Stability:

Stable at normal temperatures and storage conditions.

Conditions to Avoid:

Temperatures in excess of 200 C (392 F).

Incompatibility with Other Materials:

None reasonably foreseeable.

Hazardous Decomposition Products:

Incomplete combustion, thermal degradation and hydrocarbon oxidation generate highly toxic gases including carbon monoxide, organic acids, aldehydes, alcohols, and oxides of sodium.

SECTION XI – **Toxicological Information**

Vinyl Alcohol Polymers and Copolymers- The oral LD50 for this polymer is greater than 11000 milligrams per kilogram of body weight as determined in rats, which is extremely low toxicity. The polymer was also tested on male guinea pigs. No irritation or sensitization effects were discovered.

Glycerol-

Oral LD50:	4090 mg/kg in rats
Oral LD50:	27gm/kg in rabbits
Dermal LD50:	10gm/kg in rabbits
Inhalation 1 hour LC50:	570mg/kg in rats

Polyethylene glycol P-1,1,3,3-tetramethylbutylphenyl ether-

Oral LD50:	1800mg/kg in rats
Inhalation 1 hour LC50:	375mg/kg in rats

Acrylic Resin-

LC50 24hours:	720 mg/L in rainbow trout
LC50 96hours:	420 mg/L in rainbow trout

Methanol-

Oral LD50:	9100 mg/kg in rats
Dermal LD50:	15840 mg/kg in rabbits
Inhalation 1 hour LC50:	145000ppm in rats

Animal testing indicates Methyl Alcohol is an eye and skin irritant. Eye contact caused clouding of the eye (corneal opacity). Repeated skin contact at elevated concentrations caused some mortality. Single exposure by ingestion caused narcosis, liver effects, and hypothermia. Repeated ingestion caused pathological changes of the eyes and acidosis. Repeated exposure by inhalation caused irritation of the eyes and blindness.

SECTION XII – **Ecological Information**

This product has not been evaluated for its ecotoxicity. However, based upon degradation studies of similarly formulated dispersions, it can be concluded that most of the ingredients will degrade. The biodegradation of colorants under aerobic conditions is expected to be limited and there is not evidence to suggest they create any significant ecological problems when released into the environment. Since pigments are by design insoluble compounds, they are believed to have minimal bioaccumulation and bioavailablity characteristics.

SECTION XIII – **Disposal Considerations**

Chemical waste generators must determine whether a discarded chemical is classified as a hazardous waste. US EPA guidelines for the classification determination are listed in 40 CFR Part 261.3. Preferred options for disposal are (1) recycling, (2) incineration with energy recovery, (3) landfill. The high fuel value of this product makes option 2 very desirable for material that cannot be recycled. Treatment, storage, transportation, and disposal must be in accordance with applicable federal, state, provincial and local regulations.

SECTION XIV – **Transportation Information**

D.O.T. proper shipping name:	N/A
Hazardous Substance (49CFR):	N/A
D.O.T. Hazard Class (CFR L72.101-102):	N/A
D.O.T. Labels Required (49CFR):	N/A
D.O.T. Placards Required:	N/A
Poison Constituent:	N/A
International Regulations:	Not Regulated
UN/NA Code:	NONE
IMDG/IACO Classification:	Not Regulated
IATA Classification:	Not Regulated

SECTION XV – **Regulatory Information**

Superfund Amendments and Reauthorization Act of 1986 (SARA) Title III Section 313-

No chemicals in this product exceed the minimum reporting level established by SARA title III, Section 312 and 40 CFR 372.

Toxic Substance Control Act (TSCA)-All compontents of this product are listed on the TSCA Inventory and are in compliance for commercial purposes.

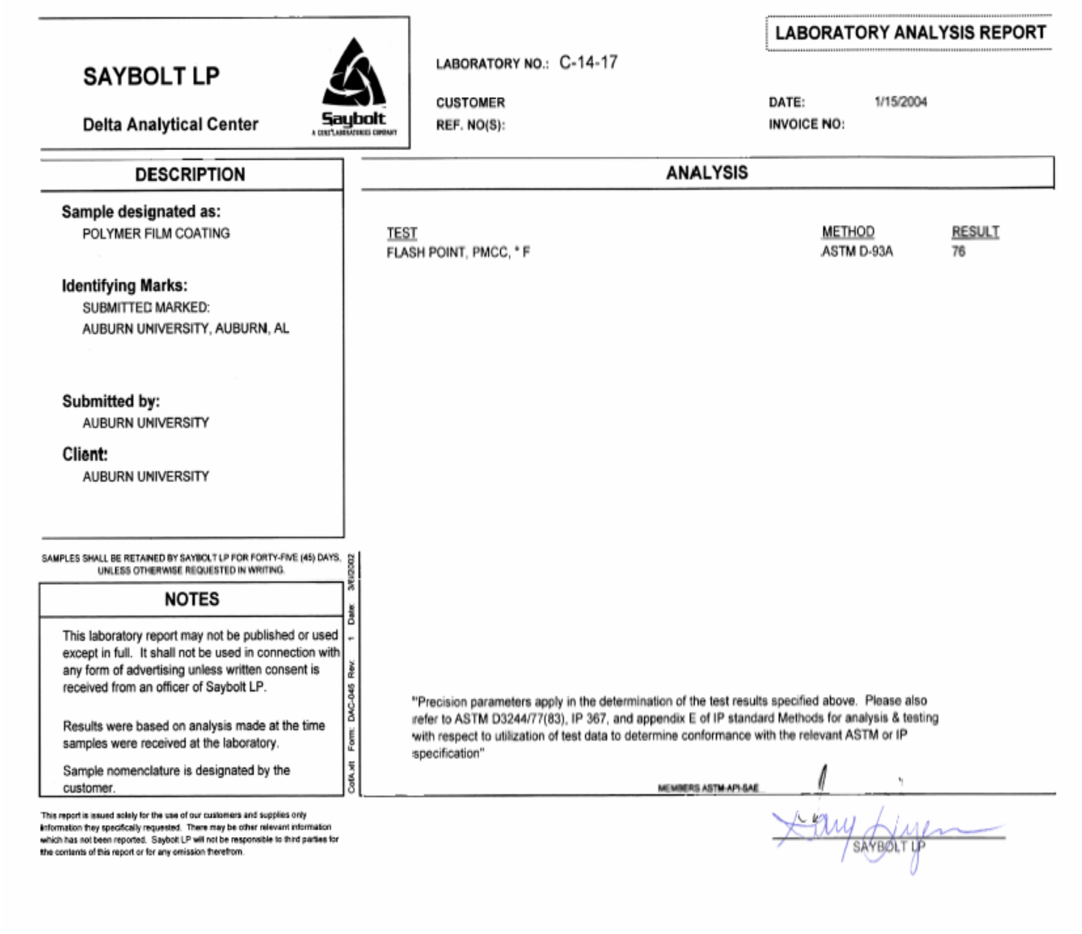
Comprehensive Environmental Response, Compensation and Liability Act (CERLA)-

No chemicals in this product are subject to the reporting requirements of CERLA. Clean Water Act (CWA)-This material does not contain any Hazardous Air Pollutants, Class 1 Ozone Depletors, Class 2 Ozone Depletors, Hazardous Substances, Priority Pollutants, or Toxic Pollutants listed under the CWA.

Disclaimer of Liability. The information above is believed to be accurate and represents the best information currently available. However, we make no warranty of merchantability or any other warranty, express or implied, with respect to such information, and we assume no liability resulting from its use. Users should make their own investigations to determine the suitability of the information for their particular purpose. In no event shall Orex be liable for any claims, losses, or damages of any third party or for lost profits or any special, indirect consequential or exemplary damages, howsoever arising, even if Orex has been advised of the possibility of such damages.

MSDS Creation Date: 07/2004

Appendix C: CLOSED CUP FLASH POINT TEST ANALYSIS



LABORATORY ANALYSIS REPORT

SAYBOLT LP

Delta Analytical Center

Saybolt

LABORATORY NO.: C-14-17

CUSTOMER REF. NO(S):		DATE:	1/15/2004
		INVOICE NO:	

DESCRIPTION

Sample designated as:
POLYMER FILM COATING

Identifying Marks:
SUBMITTED MARKED:
AUBURN UNIVERSITY, AUBURN, AL

Submitted by:
AUBURN UNIVERSITY

Client:
AUBURN UNIVERSITY

SAMPLES SHALL BE RETAINED BY SAYBOLT LP FOR FORTY-FIVE (45) DAYS, UNLESS OTHERWISE REQUESTED IN WRITING.

NOTES

This laboratory report may not be published or used except in full. It shall not be used in connection with any form of advertising unless written consent is received from an officer of Saybolt LP.

Results were based on analysis made at the time samples were received at the laboratory.

Sample nomenclature is designated by the customer.

CofA.xlt Form: DAC-045 Rev: 1 Date: 3/6/2002

This report is issued solely for the use of our customers and supplies only information they specifically requested. There may be other relevant information which has not been reported. Saybolt LP will not be responsible to third parties for the contents of this report or for any omission therefrom.

ANALYSIS

TEST	METHOD	RESULT
FLASH POINT, PMCC, ° F	ASTM D-93A	76

"Precision parameters apply in the determination of the test results specified above. Please also refer to ASTM D3244/77(83), IP 367, and appendix E of IP standard Methods for analysis & testing with respect to utilization of test data to determine conformance with the relevant ASTM or IP specification"

MEMBERS ASTM-API-SAE

SAYBOLT LP

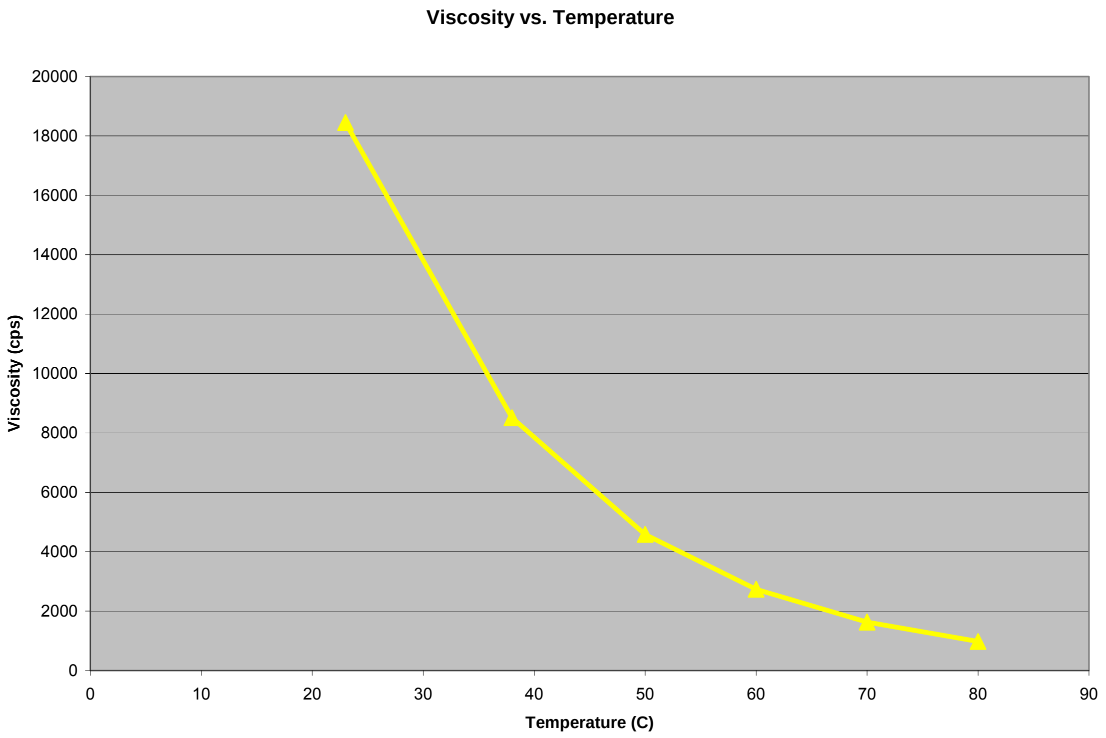
Appendix D: LIQUID VISCOSITY DETERMINATION PROCEDURES AND DATA

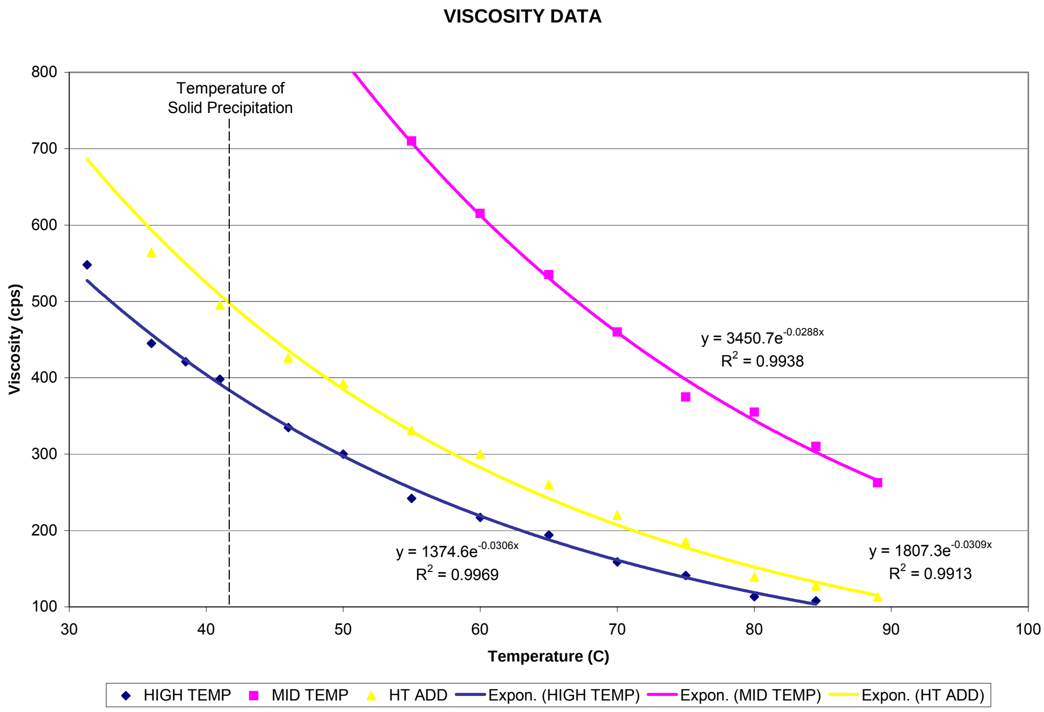
The Synchro-Lectric Viscometer rotates a cylinder or disc in a fluid and measures the torque necessary to overcome the viscous resistance to the induced movement. This is accomplished by driving the immersed element, which is called a spindle, through a beryllium copper spring—the degree to which the spring is wound, indicated by the position of the red pointer on the Viscometer's dial, is proportional to the viscosity of the fluid for any given speed and spindle.

The Viscometer is able to measure over a number of ranges since, for a given drag, or spring deflection, the actual viscosity is proportional to the spindle speed, and is also related to the spindle's size and shape. For material of given viscosity, the drag will be greater as the spindle size and/or rotational speed increase. The minimum range of any viscometer is obtained by using the largest spindle at the highest speed—the maximum range by using the smallest spindle at the slowest speed.

Measurements made using the same spindle at different speeds are used to detect and evaluate the rheological properties of the test material.

All viscosity measurements were determined using this device. Samples are provided.


Viscosity vs. Temperature
Viscosity (cps)
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
0
10
20
30
40
50
60
70
80
90
Temperature (C)


VISCOSITY DATA
Temperature of
Solid Precipitation
Viscosity (cps)
800
700
600
500
400
300
200
100
30
40
50
60
70
80
90
100
Temperature (C)
y = 3450.7e$^{-0.0288x}$
R^2 = 0.9938
y = 1374.6e$^{-0.0306x}$
R^2 = 0.9969
y = 1807.3e$^{-0.0309x}$
R^2 = 0.9913
HIGH TEMP
MID TEMP
HT ADD
Expon. (HIGH TEMP)
Expon. (MID TEMP)
Expon. (HT ADD)

Appendix E: DIFFERENTIAL SCANNING CALORIMETERY METHODS TO INVESTIGATE GLASS TRANSITION TEMPERATURES AND DATA.

Calorimetry (Differential Scanning Calorimetry, DSC; Differential Thermal Analysis, DTA):

Calorimetry involves the measurement of relative changes in temperature and heat or energy either under isothermal or adiabatic conditions. *Chemical calorimetry* where the heats of reaction are measured, usually involve isothermal conditions. *Bomb or flame calorimeters* involve adiabatic systems where the change in temperature can be translated, using the heat capacity of the system, into the enthalpy or energy content of a material such as in determination of the calorie content of food. In materials characterization calorimetry usually involves an adiabatic measurement. A calormetric measurement in materials science is carried out on a closed system where determination of the heat, Q, associated with a change in temperature, ΔT, yields the heat capacity of the material, C:

Data Interpretation:

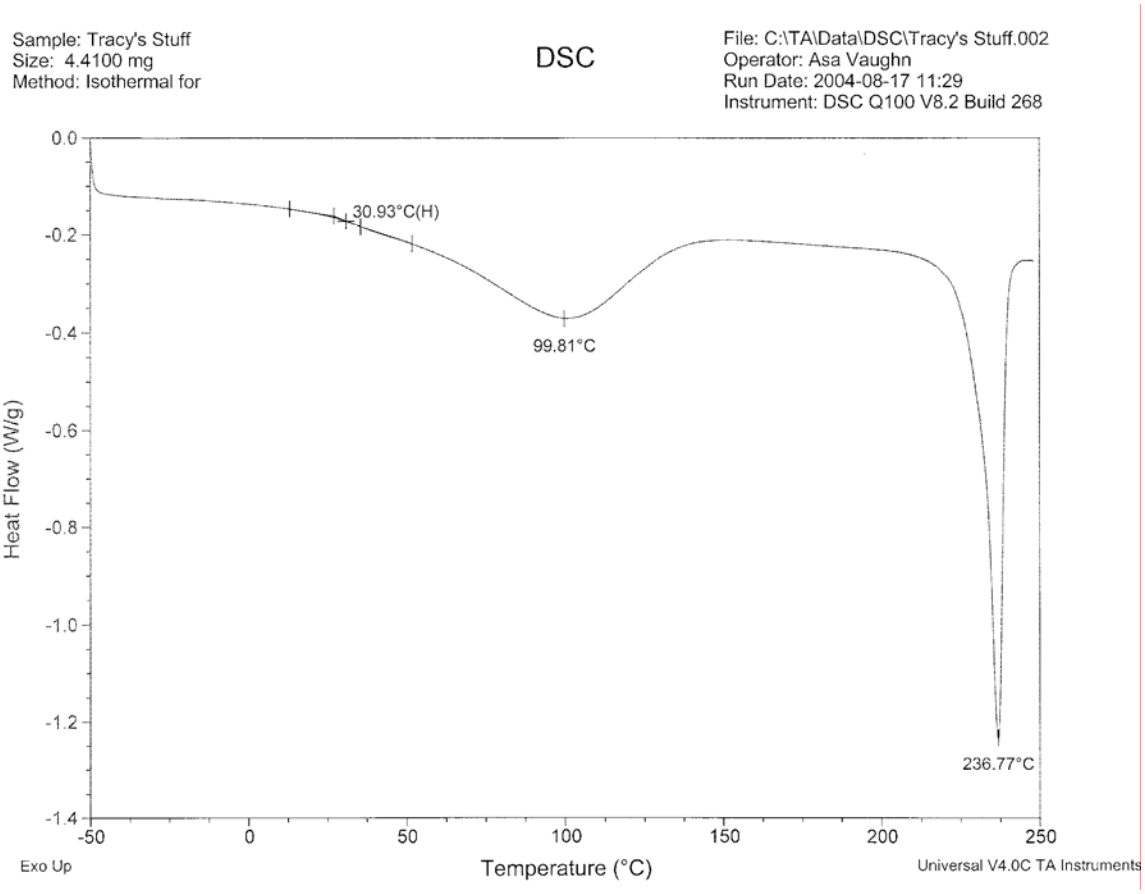
The output of a DSC is a plot of heat flux (rate) versus temperature at a specified temperature ramp rate. The heat flux can be converted to C P by dividing by the constant rate of temperature change. The output from a DTA is temperature difference (ΔT) between the reference and sample cells versus sample temperature at a specified heat flux. Qualitatively the two plots appear similar.

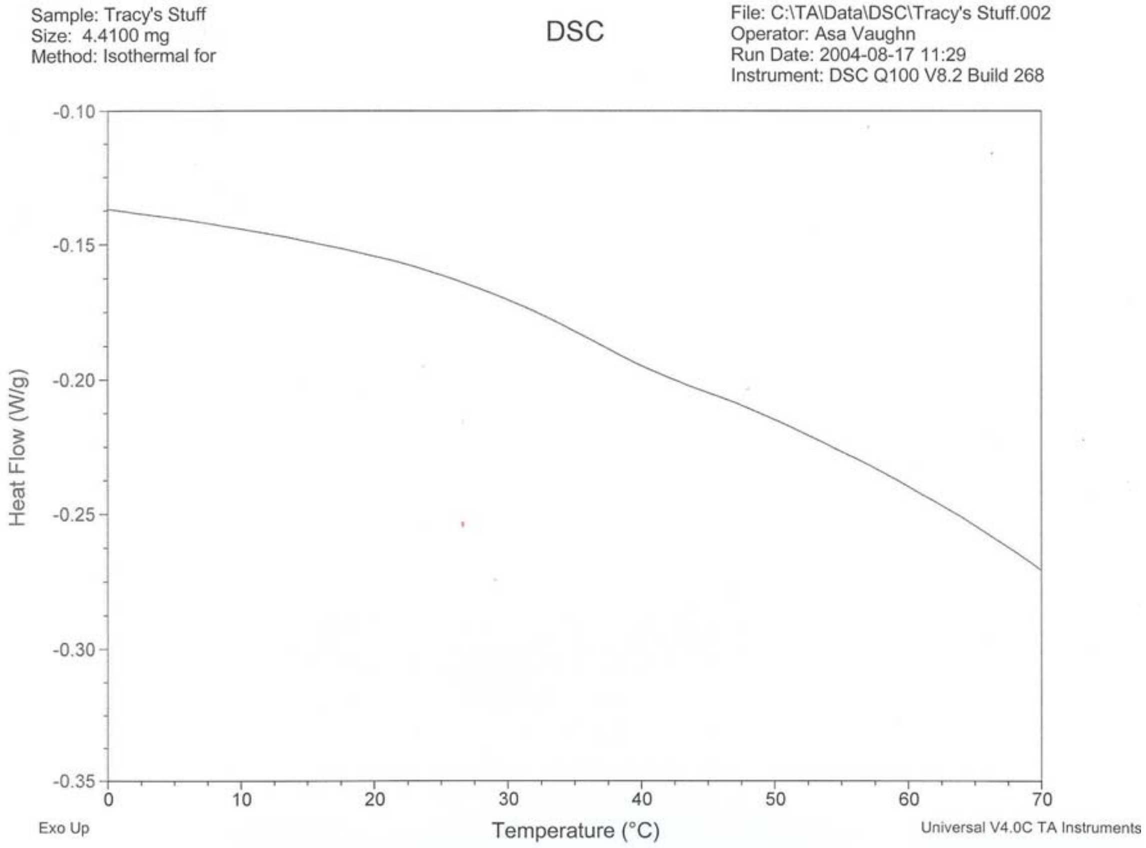
Both DSC's and DTA's must be calibrated, essentially, for each use since small changes in the sample cells (oil from fingers etc.) can significantly shift the instrumental calibration. For polymer samples these instruments are typically calibrated with low melting metal crystals that display a sharp melting transition such as indium (T m =

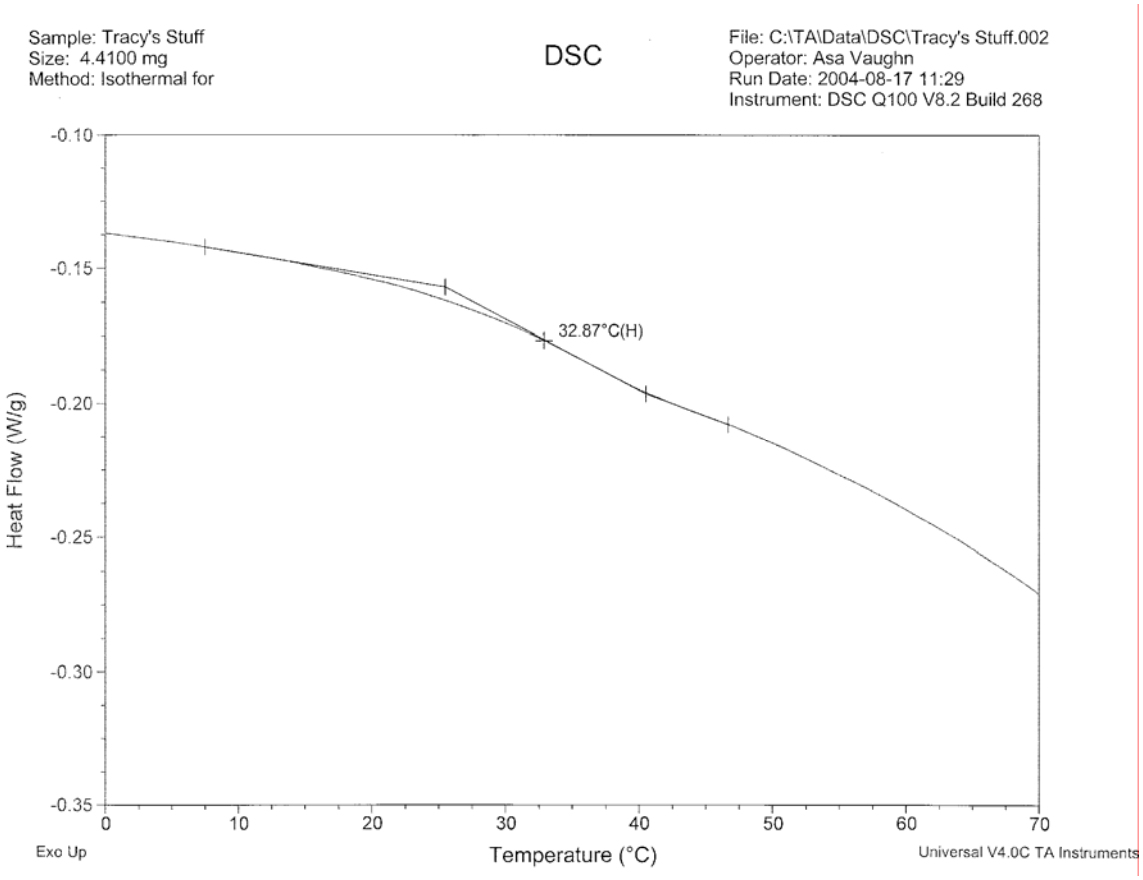
155.8°C) and low molecular weight organic crystals such as naphthalene. The volatility of low molecular weight organic crystals requires the use of special sealed sample holders.

An instrumental time lag is always associated with scanning thermal analysis. The observed transitions may be "smeared" by this instrumental time lag (typically close to 1°C at 10°/min heating rate). Some account can be made for this time lag by comparison of results from different heating rates. Often this time lag is accounted for by taking the onset of melting as the melting point rather than the peak value for sharp melting standard samples used in calibration. For polymer samples, significant broadening of the melting peak (up to 25 to 50C°) is the norm and this is associated with the structural and kinetic features of polymer melting. Typically the peak value is reported for polymer melting points. The instrumental error in temperature for a DSC is typically ±0.5 to 1.0 C°.

The data generated from the DSC testing gave crucial information about the glass transition temperatures of different polymer blends to aid in understanding the “jello-like” state that the fluid enters and the associated reanimation process. Samples of this data are provided on the following pages.

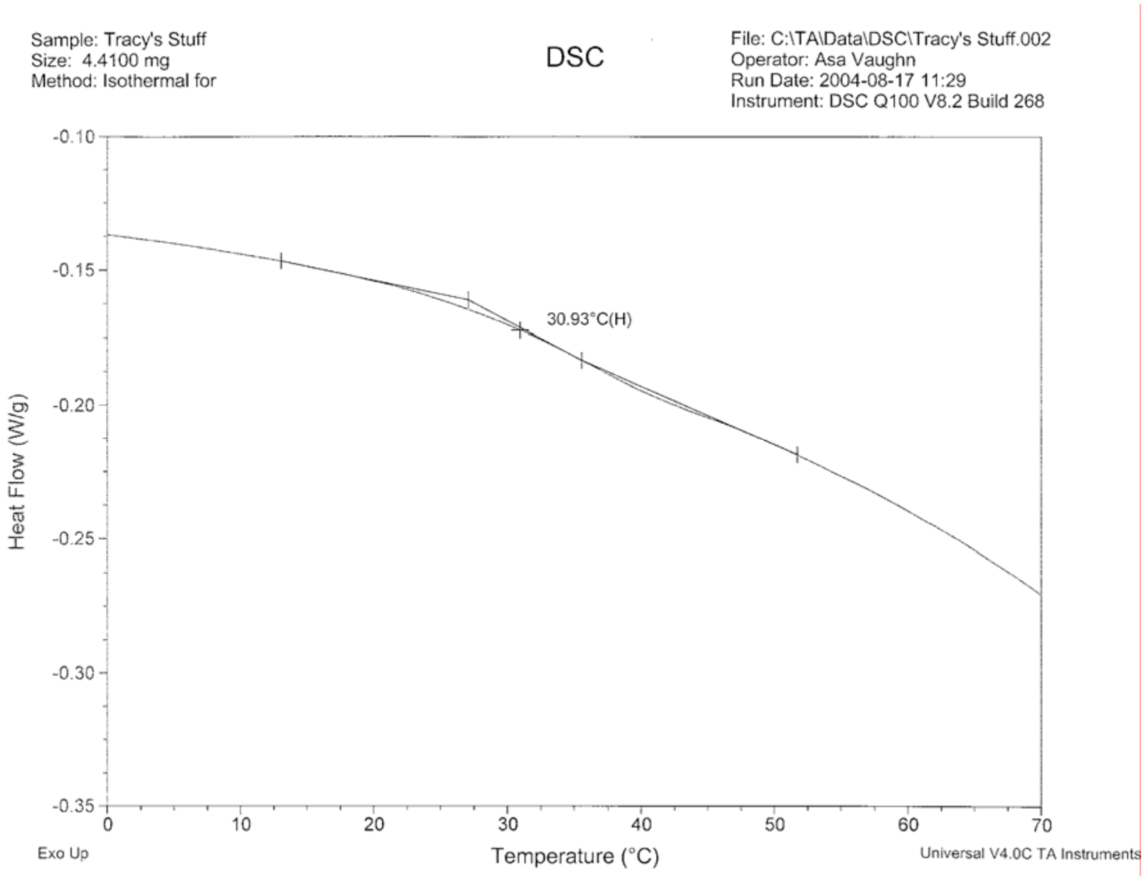

Sample: Tracy's Stuff
Size: 4.4100 mg
Method: Isothermal for
DSC
File: C:\TA\Data\DSC\Tracy's Stuff.002
Operator: Asa Vaughn
Run Date: 2004-08-17 11:29
Instrument: DSC Q100 V8.2 Build 268
0.0
-0.2
-0.4
-0.6
-0.8
-1.0
-1.2
-1.4
Heat Flow (W/g)
30.93°C(H)
99.81°C
236.77°C
-50
0
50
100
150
200
250
Temperature (°C)
Exo Up
Universal V4.0C TA Instruments

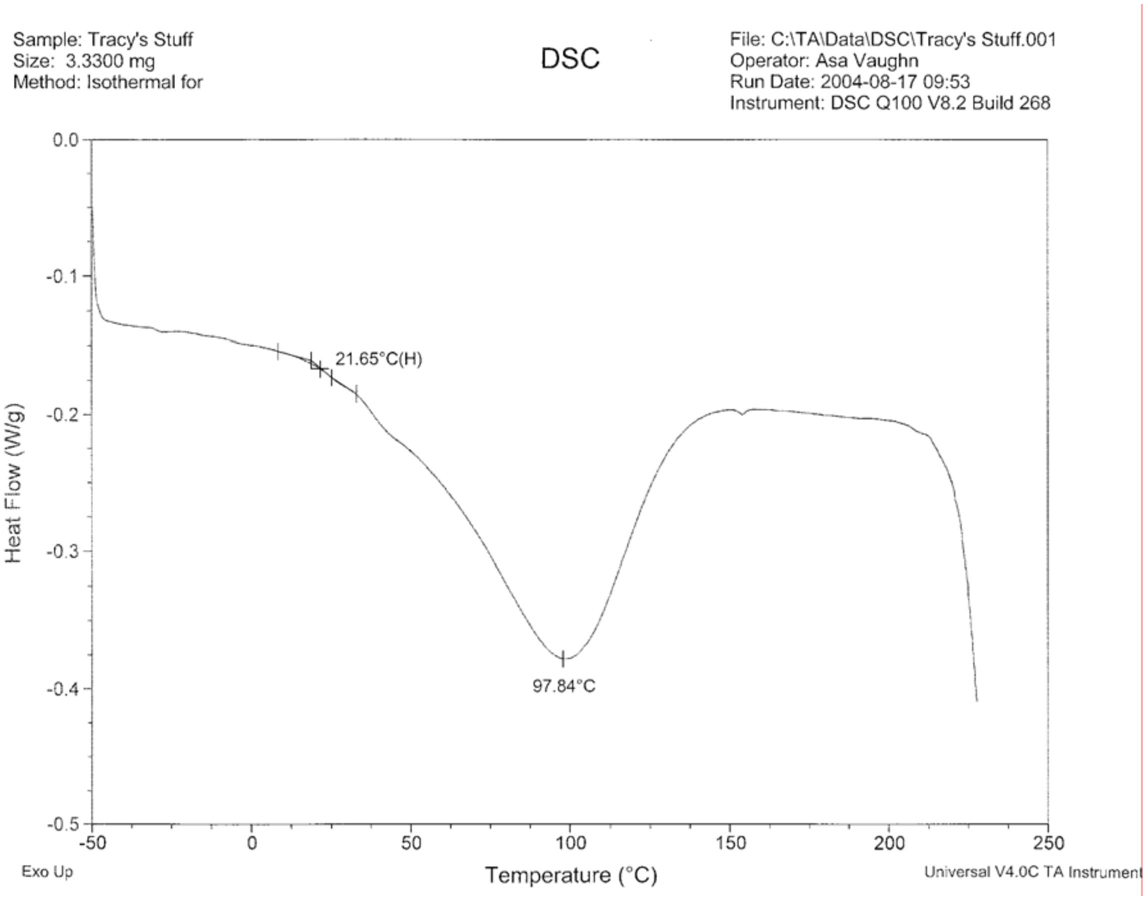

Sample: Tracy's Stuff
Size: 4.4100 mg
Method: Isothermal for
DSC
File: C:\TA\Data\DSC\Tracy's Stuff.002
Operator: Asa Vaughn
Run Date: 2004-08-17 11:29
Instrument: DSC Q100 V8.2 Build 268
-0.10
-0.15
-0.20
-0.25
-0.30
-0.35
Heat Flow (W/g)
0
10
20
30
40
50
60
70
Exo Up
Temperature (°C)
Universal V4.0C TA Instruments



Sample: Tracy's Stuff
Size: 4.4100 mg
Method: Isothermal for

File: C:\TA\Data\DSC\Tracy's Stuff.002
Operator: Asa Vaughn
Run Date: 2004-08-17 11:29
Instrument: DSC Q100 V8.2 Build 268


Sample: Tracy's Stuff
Size: 4.4100 mg
Method: Isothermal for
DSC
File: C:\TA\Data\DSC\Tracy's Stuff.002
Operator: Asa Vaughn
Run Date: 2004-08-17 11:29
Instrument: DSC Q100 V8.2 Build 268
30.93°C(H)
Heat Flow (W/g)
-0.10
-0.15
-0.20
-0.25
-0.30
-0.35
0
10
20
30
40
50
60
70
Temperature (°C)
Exo Up
Universal V4.0C TA Instruments


Sample: Tracy's Stuff
Size: 3.3300 mg
Method: Isothermal for
DSC
File: C:\TA\Data\DSC\Tracy's Stuff.001
Operator: Asa Vaughn
Run Date: 2004-08-17 09:53
Instrument: DSC Q100 V8.2 Build 268
0.0
-0.1
-0.2
-0.3
-0.4
-0.5
Heat Flow (W/g)
21.65°C(H)
97.84°C
-50
0
50
100
150
200
250
Exo Up
Temperature (°C)
Universal V4.0C TA Instrument

Appendix F: THERMAL GRAVIMETERIC ANALYSIS OF FILM CURING TIME AND DATA

This method is a simple analytical technique that measures the weight loss (or weight gain) of a material as a function of temperature. As materials are heated, they can loose weight from a simple process such as drying, or from chemical reactions that liberate gasses. Some materials can gain weight by reacting with the atmosphere in the testing environment. Since weight loss and gain are disruptive processes to the sample material or batch, knowledge of the magnitude and temperature range of those reactions are necessary in order to design adequate thermal ramps and holds during those critical reaction periods.

Characteristics or Properties Measured

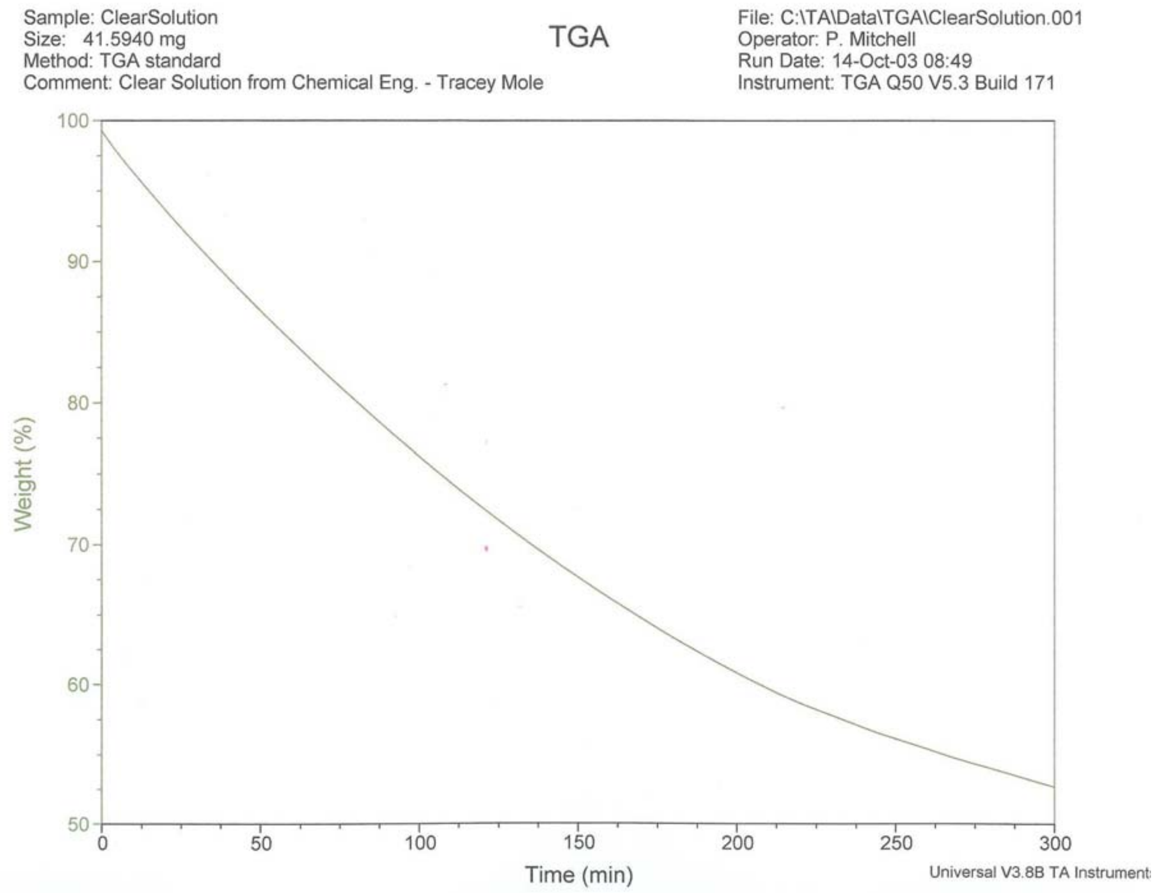
Drying, structural water release, structural decomposition, carbonate decomposition, gas evolution, sulfur oxidation, fluoride oxidation, and re-hydration.

Examples of Applications

The test results are a graph of the TGA signal (actual weight loss or gain converted to percent weight loss) on the Y-axis plotted versus the sample temperature in °C on the X-axis. Sample graphs of enhanced standard outputs are shown below.

TGA - Principle of Operation

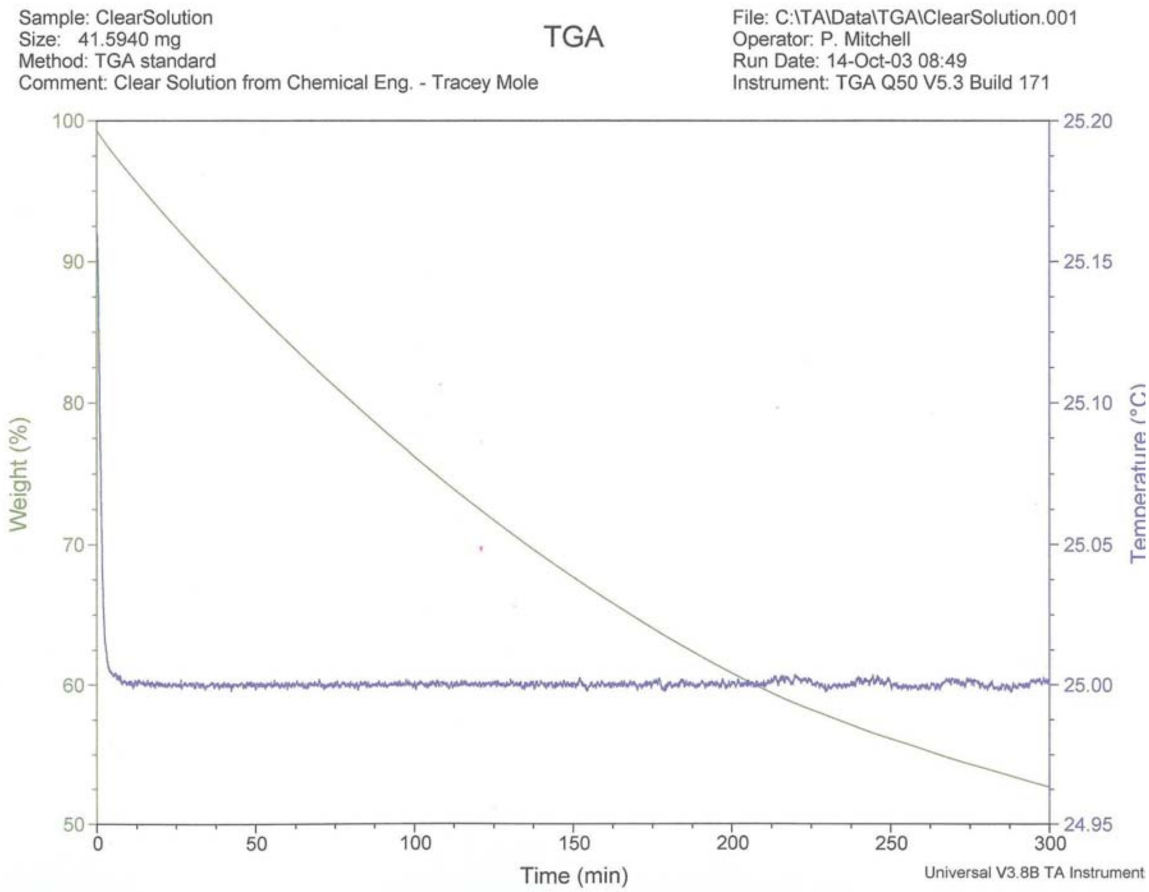
A sample of the test material is placed into a high alumina cup that is supported on, or suspended from an analytical balance located outside the furnace chamber. The balance is zeroed, and the sample cup is heated according to a predetermined thermal cycle. The balance sends the weight signal to the computer for storage, along with the sample temperature and the elapsed time. The TGA curve plots the TGA signal, converted to percent weight change on the Y-axis against the reference material temperature on the X-axis. Current manufactures two basic types of TGA instruments. One uses a standard pan balance in which the sample cup is supported by a ceramic post sitting on the balance pan, and the other uses a higher resolution balance that suspends the sample cup from overhead.



Sample: ClearSolution
Size: 41.5940 mg
Method: TGA standard
Comment: Clear Solution from Chemical Eng. - Tracey Mole

TGA

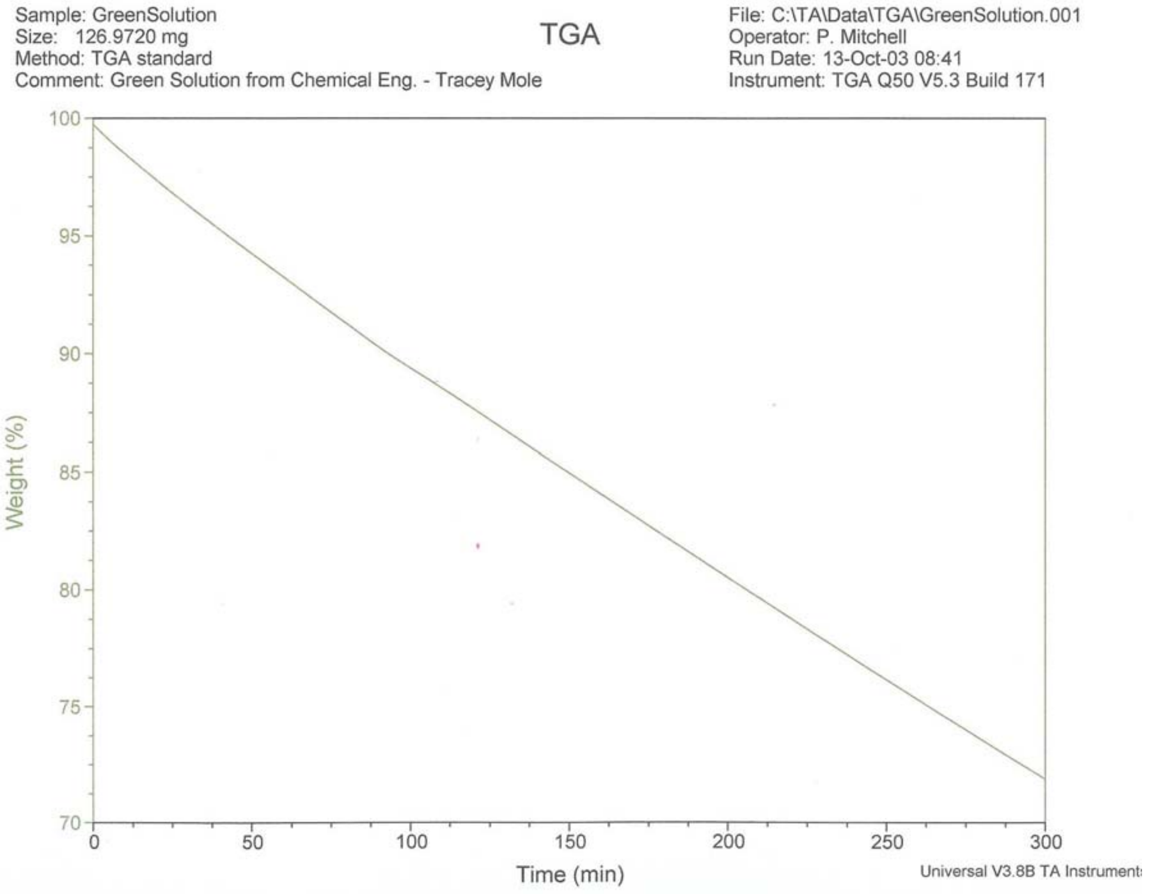
File: C:\TA\Data\TGA\ClearSolution.001
Operator: P. Mitchell
Run Date: 14-Oct-03 08:49
Instrument: TGA Q50 V5.3 Build 171



Sample: ClearSolution
Size: 41.5940 mg
Method: TGA standard
Comment: Clear Solution from Chemical Eng. - Tracey Mole

TGA

File: C:\TA\Data\TGA\ClearSolution.001
Operator: P. Mitchell
Run Date: 14-Oct-03 08:49
Instrument: TGA Q50 V5.3 Build 171



Sample: GreenSolution
Size: 126.9720 mg
Method: TGA standard
Comment: Green Solution from Chemical Eng. - Tracey Mole

TGA

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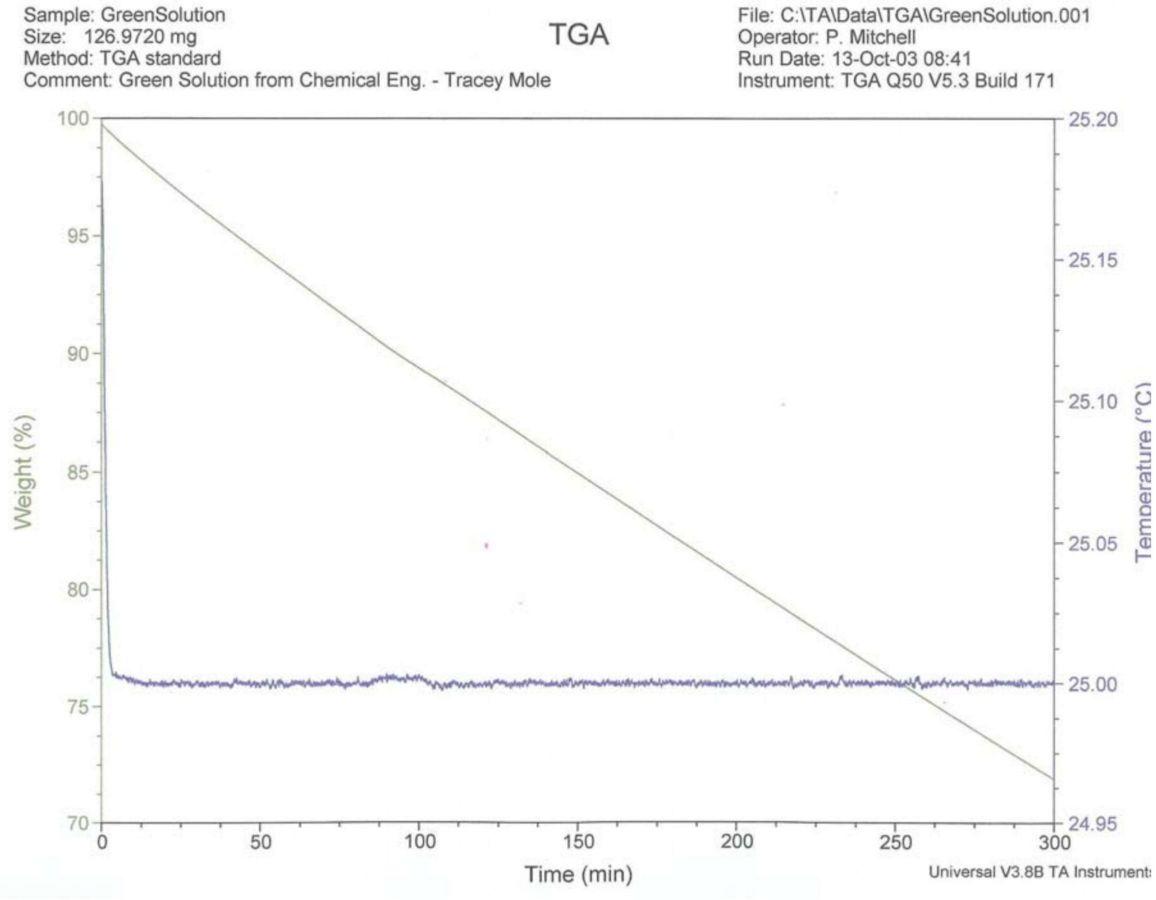
Operator: P. Mitchell
Run Date: 13-Oct-03 08:41
Instrument: TGA Q50 V5.3 Build 171



Sample: GreenSolution
Size: 126.9720 mg
Method: TGA standard
Comment: Green Solution from Chemical Eng. - Tracey Mole

TGA

File: C:\TA\Data\TGA\GreenSolution.001
Operator: P. Mitchell
Run Date: 13-Oct-03 08:41
Instrument: TGA Q50 V5.3 Build 171