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Leaching Studies on Novolac Resin Coated Proppants- Performance, Chemical Composition, Regulatory, Environmental Health, and Safety Considerations

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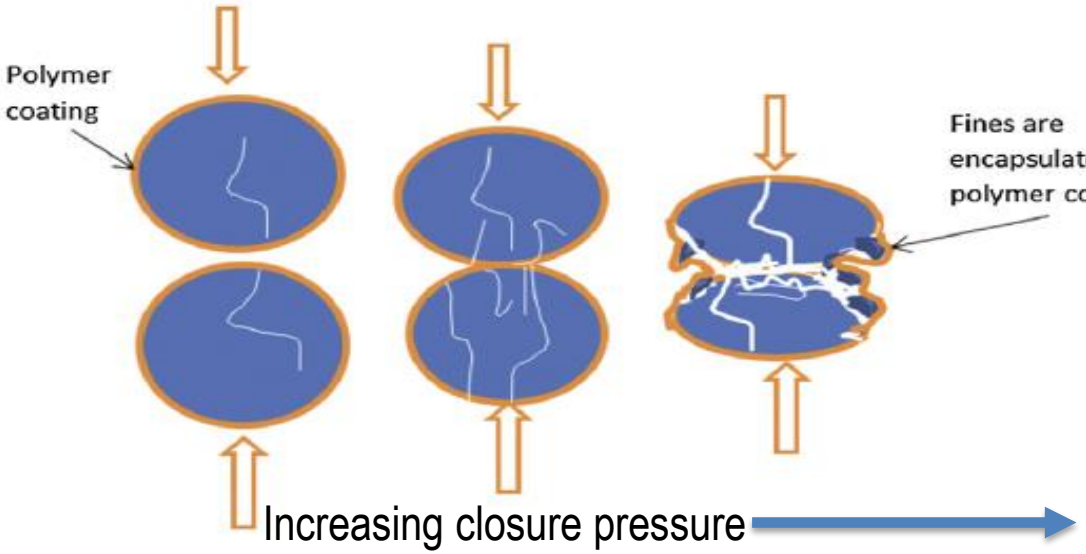
Presentation Outline

- **Introduction**
  - Why Resin-Coated Proppants (RCPs and their unique performance attributes)
  - Novolac Resin Coated Proppants for high performance fracing
  - RCP Leaching Studies in Aqueous Media-Rationale
- **Objective & Scope- Leaching Study**
  - Performance- Coating Integrity and Chemical Stability
  - Product Safety and EHS Considerations
  - Address environmental concerns specific to Novolac RCPs as well as Hexamethylenetetramine (Hexa)-cured and uncured Novolac resins (Mainly Phenol and Formaldehyde)
- **Leachate Monitoring/RCP Analysis**
  - RCP examination- LOI (Loss on Ignition) and SEM.
  - Proton NMR analysis of aqueous Leachates- Leachant Identification/Quantification
  - UV/Vis. Spectrophotometry- Quantitative Determination specific to free Phenol and other “Phenolics” in the aqueous leachates
- **Results & Discussion**
- **Summary**

Why Resin-Coated Proppants?

- Enhanced Crush Resistance via substrate protection- encapsulation of fines by polymer coating → suitable for high closure pressure (≥8 kpsi) downhole conditions.
- Can be tailored as Pre-Cured or Curable based on required performance criteria (high strength, high permeability, high temperature resistance, proppant flowback control, etc.).
- Thoughtful, complex designs of resin formulations and coating processes are required to render RCPs successful in hydraulic fracturing operations.



Zoveidavianpoor & Gharibi, *Journal of Natural Gas Science And Engineering*, **2015**, 24, 197-209.

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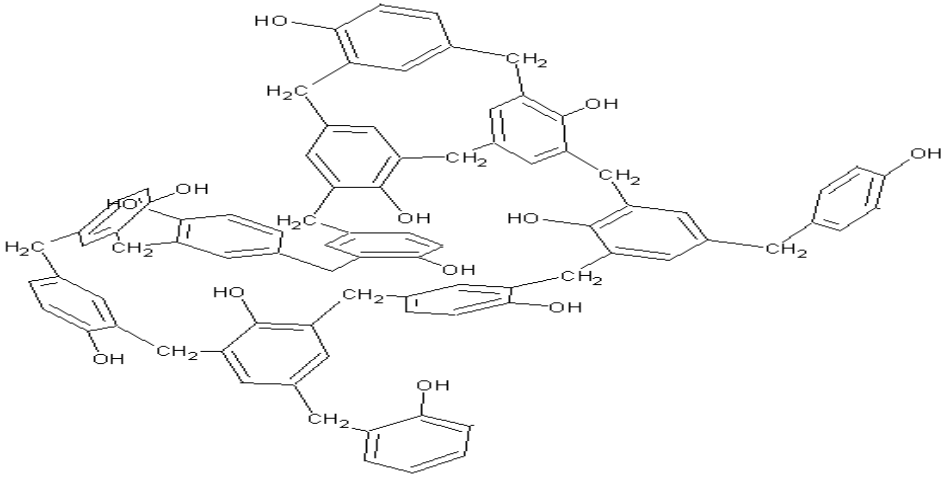
Novolac Resins for Proppant Manufacture for O & G

- Among the many application markets very favorable for the utilization of phenolic Novolacs, hydrofracing involving shale in O & G is among the most prominent.*
- Novolac RCPs constitute an important class of high performance proppants for O & G- eminently suited for the high temperature (250^{0}F), high pressure (≥ 8 Kpsi) downhole environments in hydraulic fracturing operations.
- Nuances in Novolac resin molecular architecture design and sand coating processes can lead to a variety of pre-cured and curable RCPs to address a range of hydraulic fracturing requirements.

* Pilato, L. "Phenolic resins: 100 years and still going strong", *Reactive and Functional Polymers,* **2013**, *73*, 270-77.



Hexamethylenetetramine (Hexa)-Cured Novolac Network Structure

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RCP Leaching Studies in Aqueous Media- Rationale

- Compatibility with and stability in the frac fluid media are critical to the performance of the RCP in hydraulic fracturing.
- Leaching study is a laboratory methodology to probe the interactions of the various resin systems used for proppant coating with chemicals/fluid systems mimicking downhole conditions.
- Emphasis of the leaching study on pH neutral, acidic or basic conditions generally prevalent in the fracturing fluids as well as elevated temperatures encountered in deeper wells.
- Helps develop understanding of failure mechanisms of proppants under stringent downhole conditions → Design of proppants with superior long-term performance.
- Levels of leaching have implications for product performance/integrity, product safety, and environmental health (EHS considerations).

Objective & Scope- Novolac RCP Leaching Study

Novolac RCP Leaching study in different pH environments at elevated temperatures:

- Performance indicator- Coating Integrity and Chemical stability.
- EHS Considerations- Product Safety and Environmental Health.
- Proactively address Industry's environmental concerns specific to the utilization of Novolac RCPs, and for comparison, hexa-cured and uncured Novolac resins themselves.

Leachants (Analytes) of specific concern targeted for analysis in this leaching study:

- Free Phenol* and other phenolic components.
- Formaldehyde**.

Regulatory (Examples):

*"Not-to-exceed level" determined by EPA of a lifetime exposure to 2 mg/L (2 ppm) of phenol in drinking water. "Toxicological Profile for Phenol", ATSDR, 2008, Chapter 1, pp. 1-8).

Interestingly, how can we square the above with this ??????????

** Permissible Exposure Limit (PEL) for formaldehyde according to OSHA is 0.75 ppm in air as an 8 hr. time-weighted average and short term exposure limit (STEL) of 2 ppm for 15 min. (OSHA Fact Sheet, OSHA 20007b 29 CFR 1910.1048).

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FMSA Novolac Resin Coated Proppants- Leaching Study

Sample Description:

- Two Production Batches of Novolac RCPs were investigated from a leaching study viewpoint.
- One of them was Pre-Cured (**RCP-PC**); the other was Novolac RCP with engineered Curability (RCP-Curable or **RCP-C)** during the coating process.

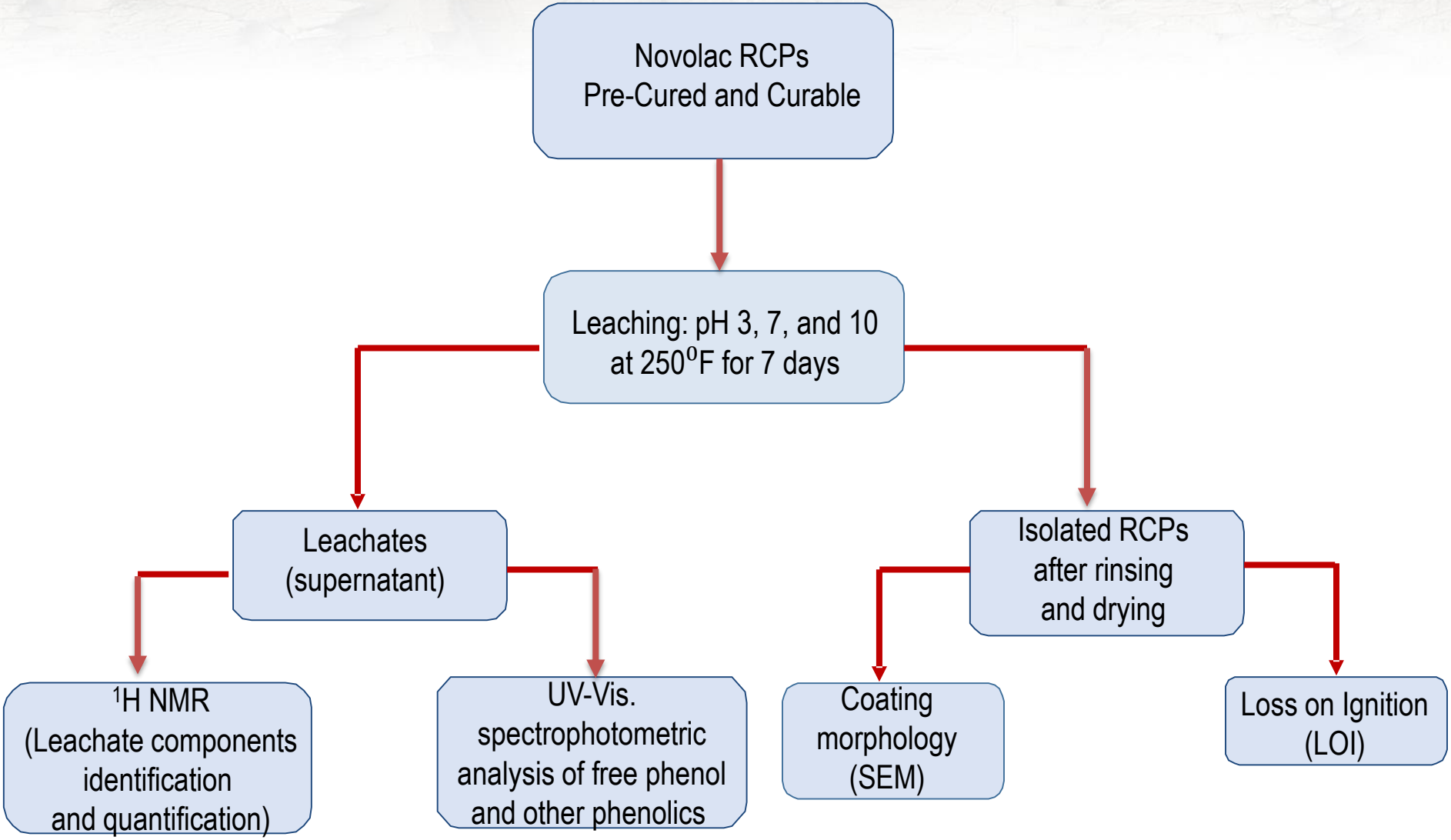
Proppant Leaching: Experimental Conditions

- pH levels at 3, 7, and 10 in aqueous media.
- Oven Temperatures at 150 & 250ºF, duration: 7 days.
- Quantities: RCP/Fluid 100g/100 ml (~8 ppa level) taken up in glass pressure bottles with polytetrafluoroethylene (**PTFE**) bushing.

Analytical/Characterization Results:

- Analysis of Proppant particles, as-coated, and after isolation/recovery from the leaching experiment.
- Analysis of the aqueous leachates (supernatants).

Leachate Monitoring and RCP Analysis- Fairmount Santrol Test Matrix



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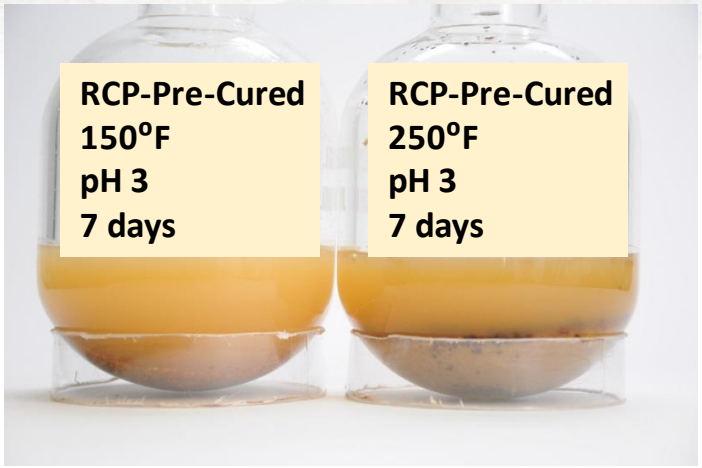
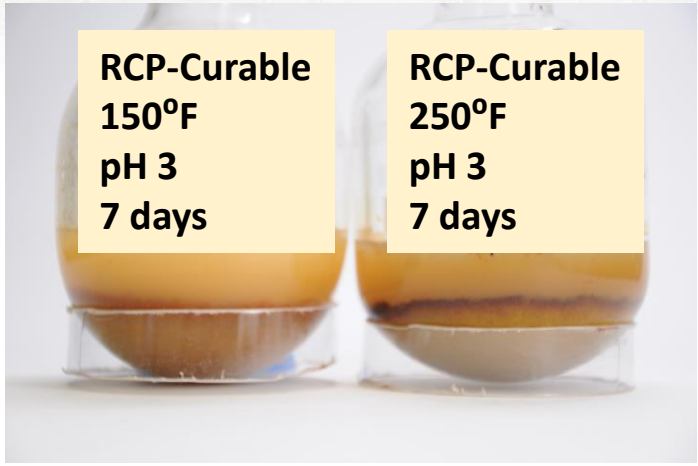
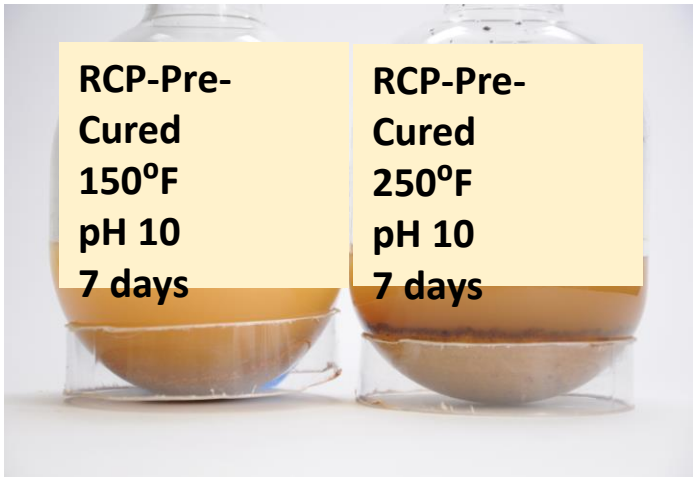
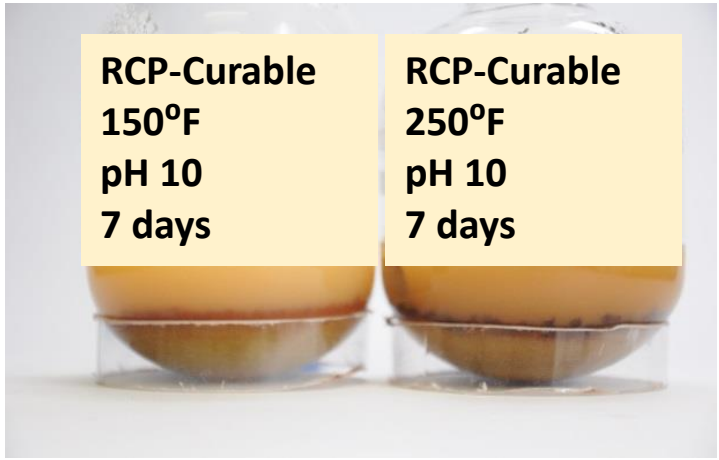
Novolac RCP Leaching- Different pH Conditions & Temperatures









Leaching under pH 3 and pH 10 conditions shown here representatively.

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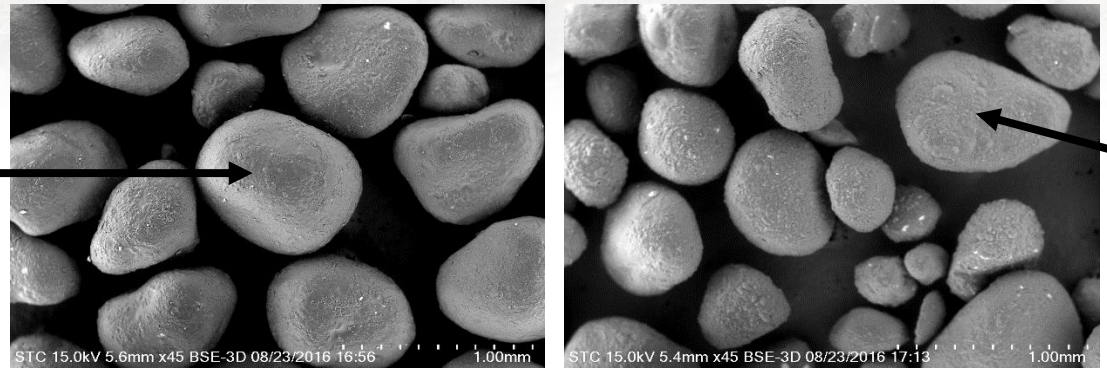
Table 1: Loss on Ignition (LOI) Analysis of the RCPs after Leaching

Resin Type For Coated Sand	RCP ID	Leaching Conditions (Temperature, Duration)	% LOI Reduction*		
			pH 3	pH 7	pH 10
Novolac	RCP-PC	150°F, 7 Days	2.9	2.4	0.0
	RCP-C	150°F, 7 Days	5.8	5.1	5.8
	RCP-PC	250°F, 7 Days	0.0	-2.2	0.0
	RCP-C	250°F, 7 Days	0.0	1.1	2.2

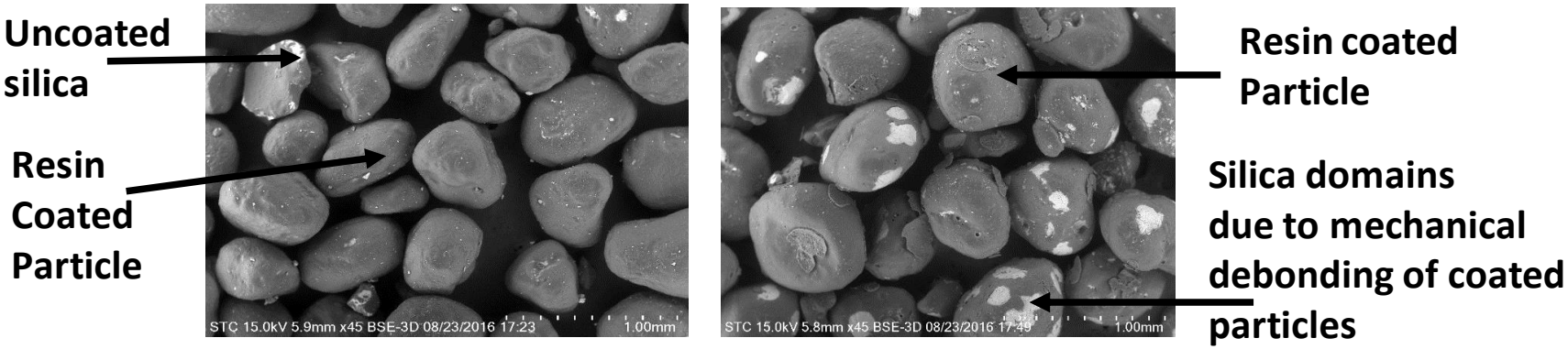
*In comparison to the LOIs measured on the as-coated RCP samples.

- Minimal changes, if any, in the LOI values-Indicative of coating stability.

Typical SEM Images- Novolac RCPs As-Coated and the RCPs after Leaching (pH 3, 250°F, 7 days)



RCP-PC (As-Coated) (a) RCP-PC (Post-Leaching)



RCP-C (As-Coated) (b) RCP-C (Post-Leaching)

- Backscattered Electron-Imaged SEMs indicative of coating integrity for the Novolc RCPs.
- Silica domains seen in RCP-C post-leaching from the rupture of inter-particle bonding in the consolidated curable proppant.

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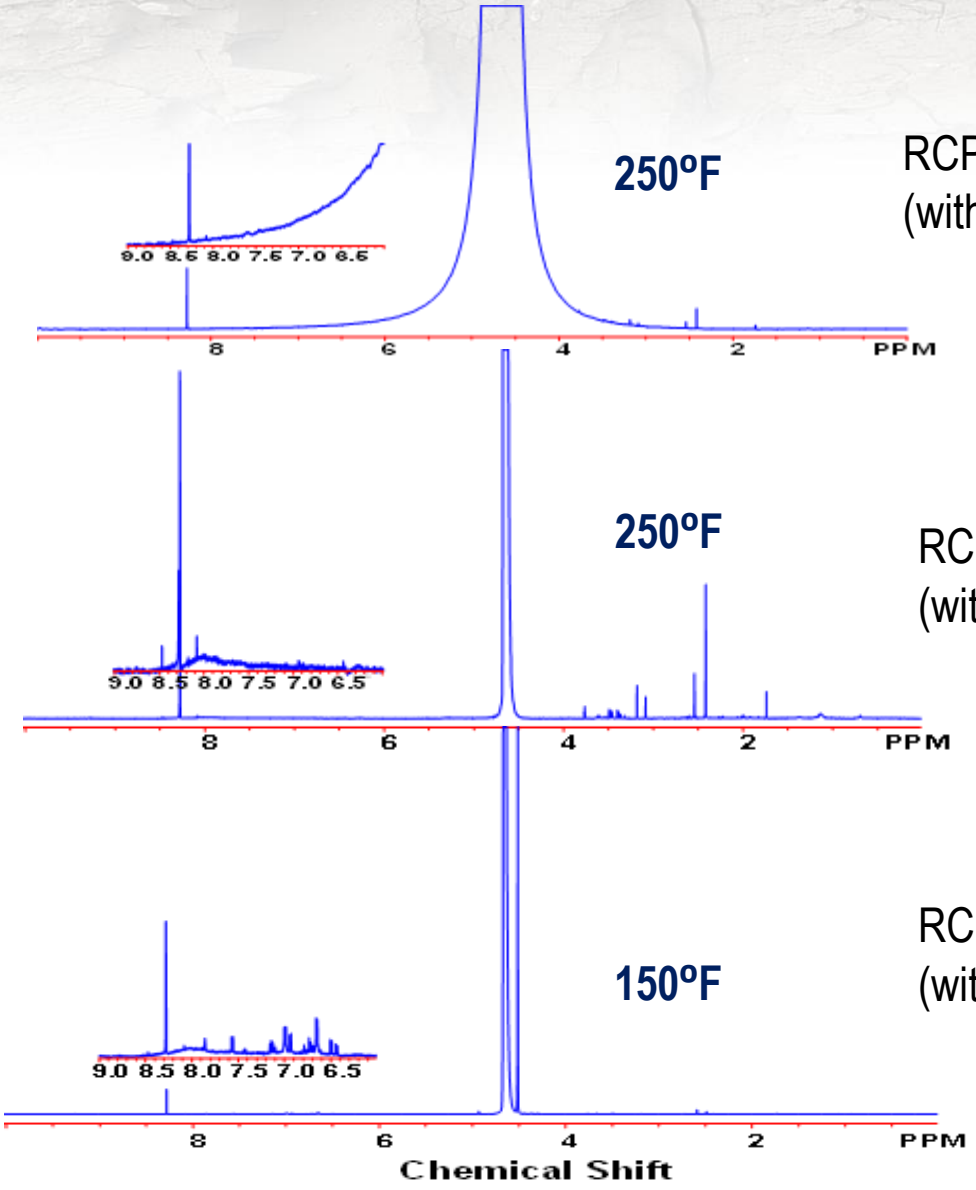
Novolac RCP Aqueous Leachate Analysis via ^{1}H NMR Spectroscopy

- Agilent high field NMR spectrometer operating at 500 MHz.
- Spectra were acquired with added D_2O.
- In-house developed methodology incorporated water 'suppression' techniques to mitigate the masking effect due to the intense, overwhelming proton signal from the presence of water.
- Appropriate pulse sequences for quantitative ^{1}H NMR data acquisition and water suppression[1,2] were employed for the detection and quantification of the very dilute species (leachants) in the aqueous leachates from the RCPs.

1. McKay, R. T. "Recent Advances in Solvent Suppression for Solution NMR: A Practical Reference", *Annual Reports on NMR Spectroscopy*, **2009,** 66, 33-76.

2. Ogg, R. J. et al., "WET, a T_1- and B_1-Insensitive Water Suppression Method for *in vivo* Localized ^{1}H NMR Spectroscopy", *Journal of Magnetic Resonance*, **1994,** series B 104, 1-10.

^{1}H NMR Spectra for Identification/Quantification of Aqueous Leachates



RCP-PC (250°F, pH 3, 7 days): ^{1}H NMR (without water suppression)

RCP-PC (250°F, pH 3, 7 days): ^{1}H NMR (with water suppression)

RCP-PC (150°F, pH 3, 7 days): ^{1}H NMR (with water suppression)

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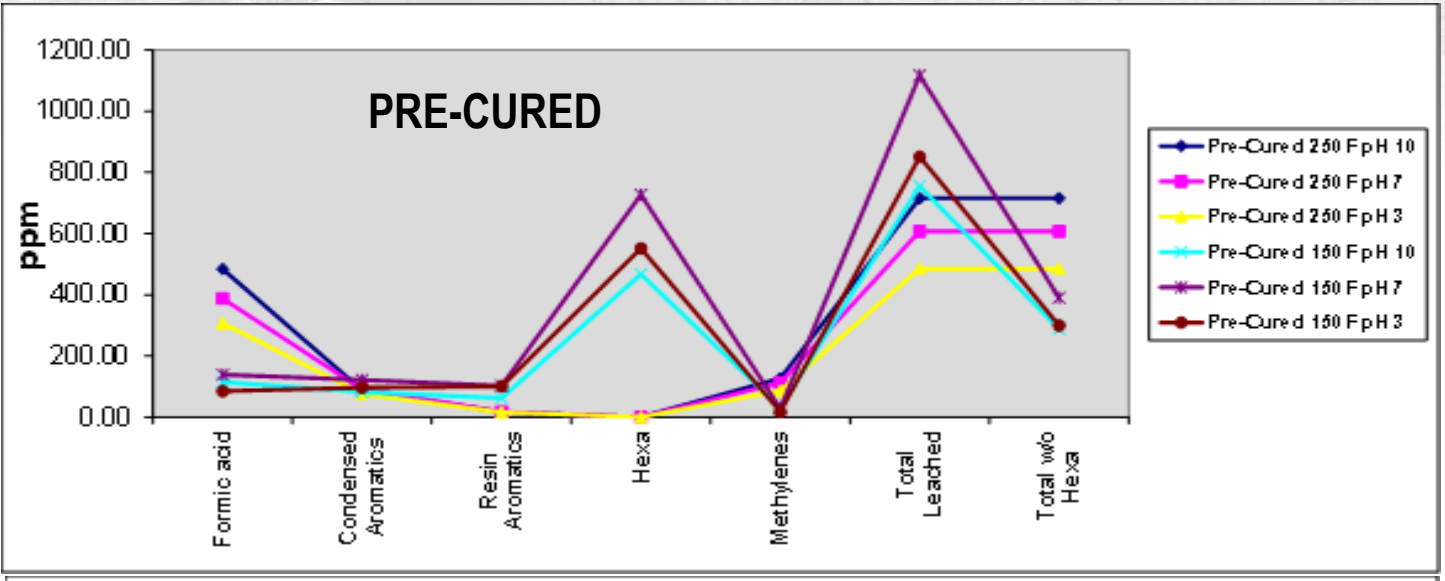
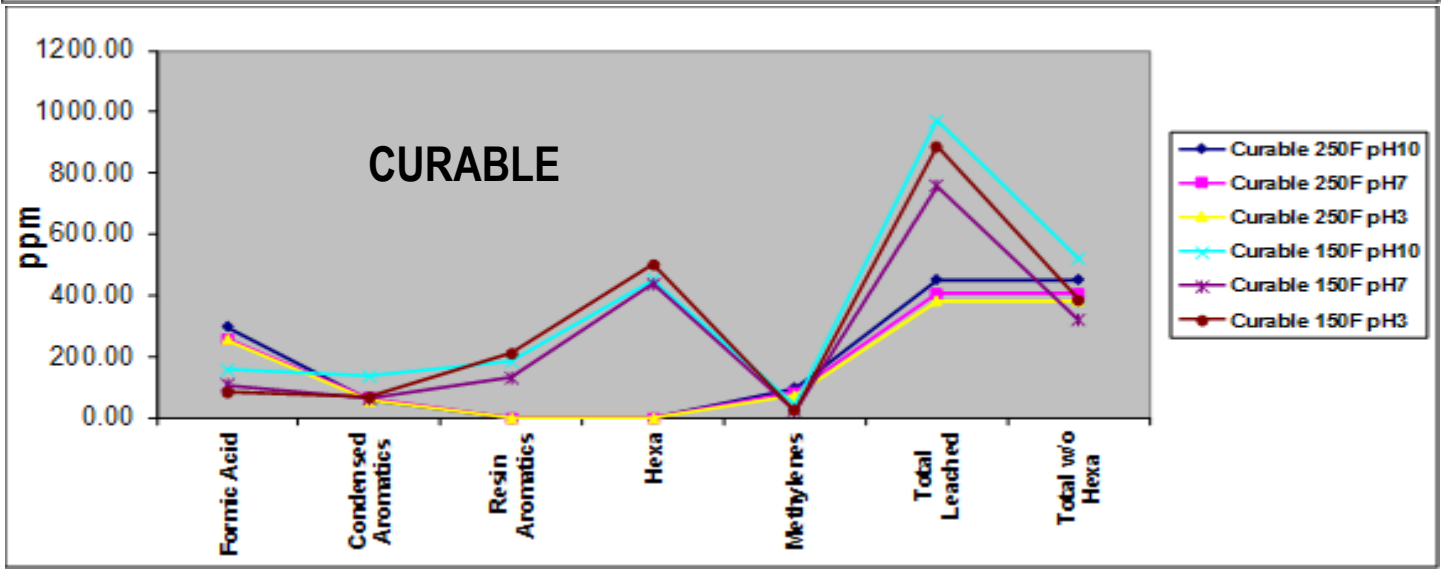
Composite Leaching Profiles: NMR Analyses of Aqueous Leachates from RCP-PC and RCP-C





- Leachates mainly contain formic acid (higher levels observed at 250ºF).
- Low to negligible levels of resin aromatics indicate low levels of phenolics including free phenol.
- Leachates from 150ºF experiments show 400-600 ppm levels of Hexa (absent at 250ºF).
- No detectable formaldehyde in the free or hydrated form.

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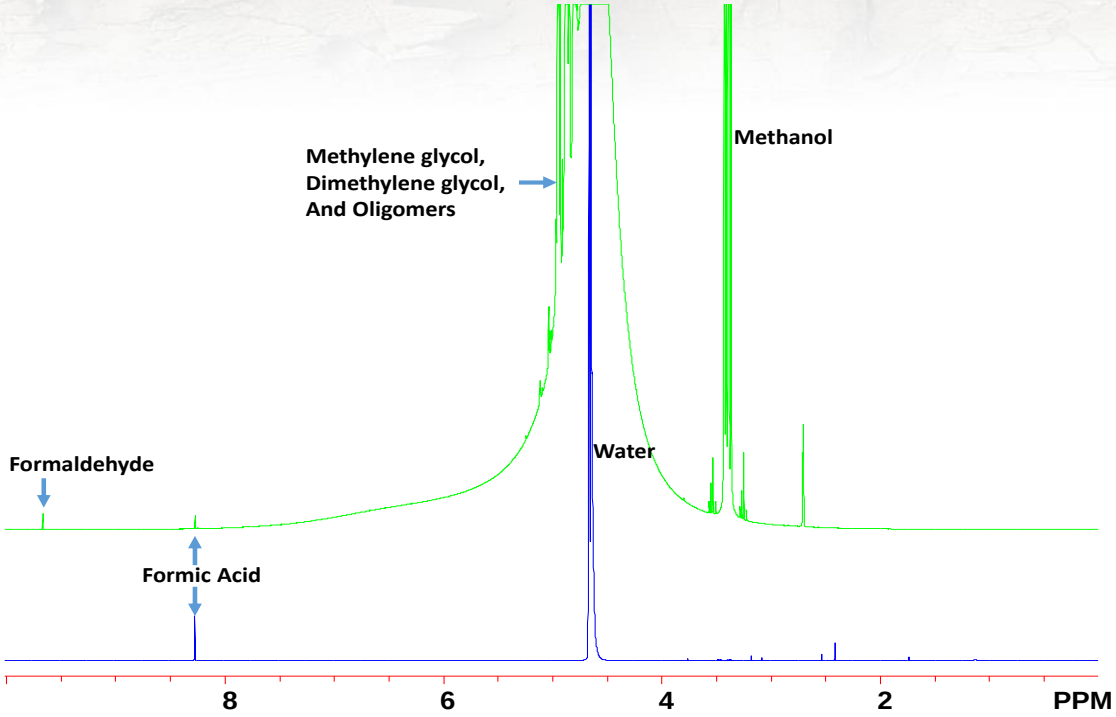
Formaldehyde Analysis in the Aqueous Leachates



Chemical Shift

Top Spectrum: Commercial formalin (37% formaldehyde in water).

Bottom Spectrum (taken with water suppression): 250^{0}F Leachate from RCP-PC (pH 3, 7 days).

- In 37% commercial formaldehyde, a weak signal at 9.7 PPM is seen for free formaldehyde.
- In water, formaldehyde predominantly exists in its hydrated form as methylene glycol and to a smaller degree, as dimethylene glycol.
- In the aqueous RCP leachate, formaldehyde cannot be detected in NMR (up to the instrument sensitivity limits) in free formaldehyde or methylene glycol form.

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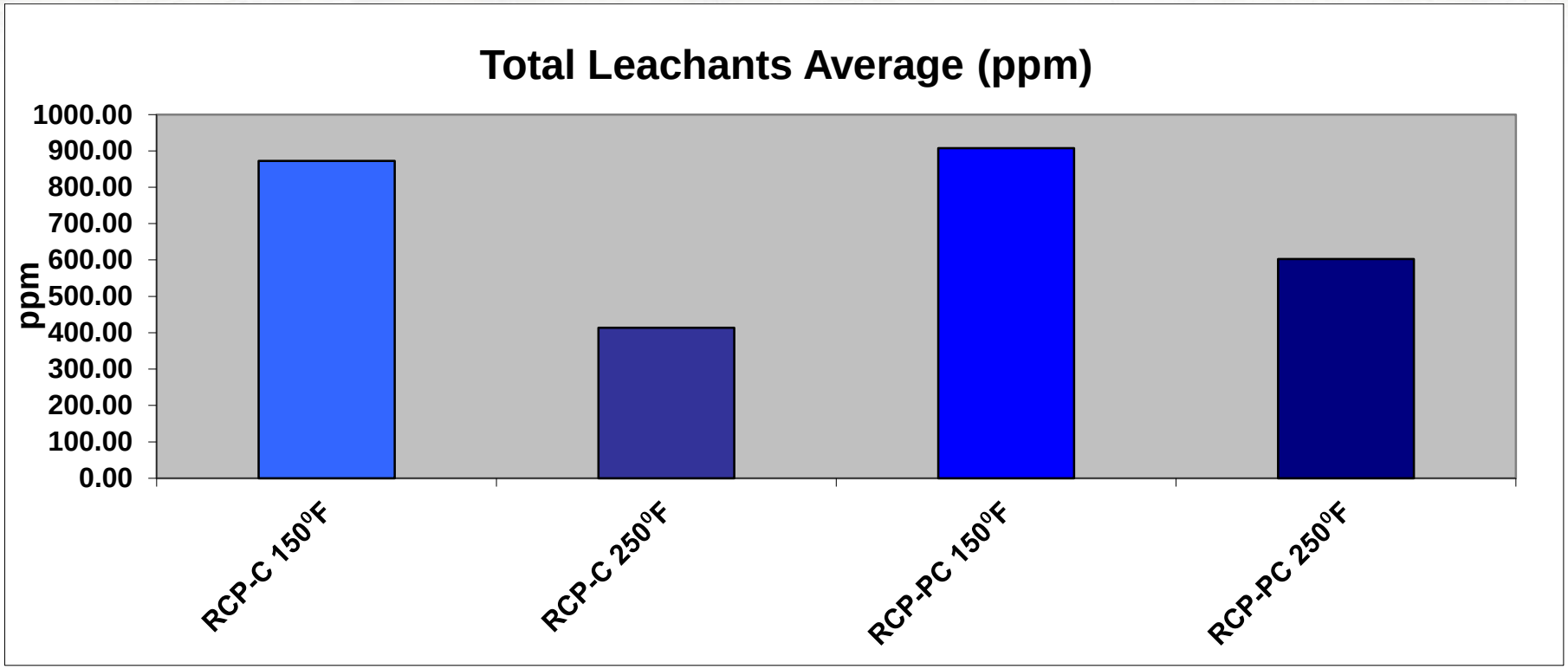
Total Leachant Avearge Levels for the two Novolac RCPs in this Study



- Total leachants amounts relatively insensitive to the three pH levels used.
- Could be averaged over three different pH levels in these experiments.
- Overall higher leachants levels at 150°F mainly due to hexa leaching which is significantly absent due to its decomposition at the higher (250°F) temperature.

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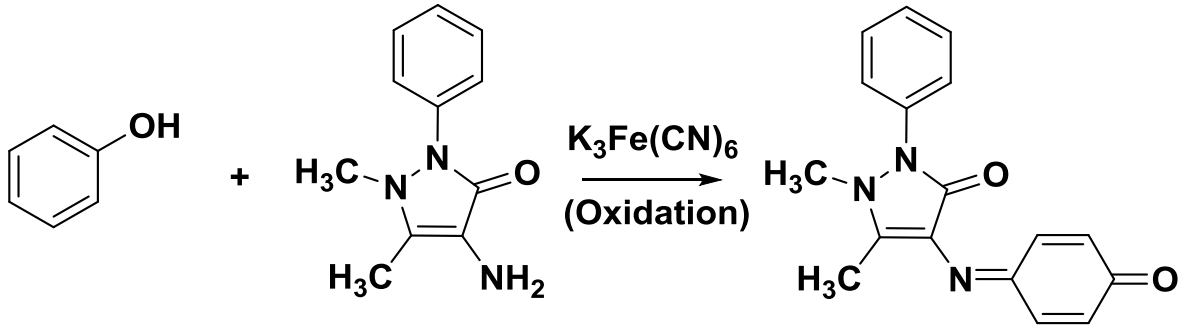
UV-Vis. Spectrophotometric Analysis: Specific to Free Phenol and Other "Phenolics"

- Sensitive protocol based on "Standard Test Methods for Phenolic Compounds in Water", ASTM International D1783-01, May 2001.
- Phenol detection and quantification-based on the absorbance of the reddish violet phenol-4-aminoantipyrine dye oxidative adduct with λ_{max} at 510 nm.



4-aminoantipyrine p-quinoneimide adduct

Scheme depicting the colored oxidative adduct for phenol detection/quantification in the presence of potassium ferricyanide (oxidizing agent)

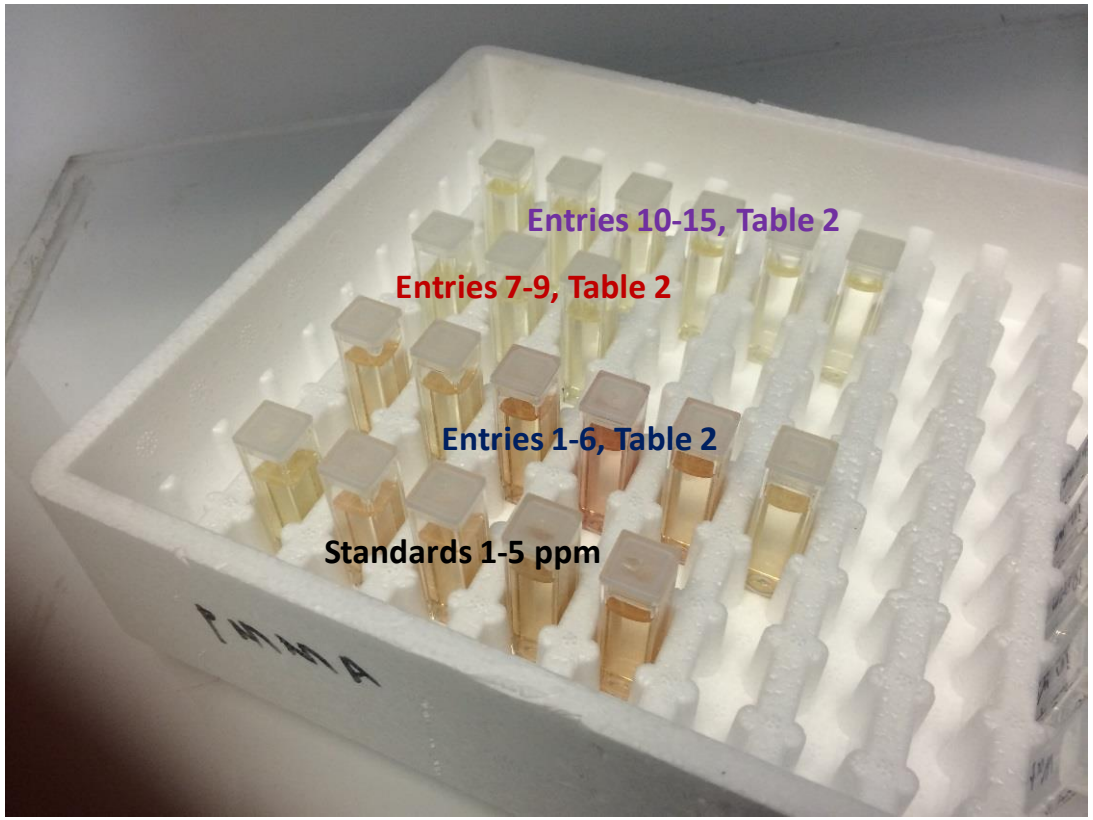
- This test applies to free phenol and also phenolic resin oligomers (dimers, trimers etc.), with open p-positions for oxidative coupling with the dye.

Table 2: "Phenolics" Detection and Quantification-Spectrophotometric analysis of Aqueous Leachates from Novolac RCPs, Hexa-Cured, and Uncured Novolac Resins.

Entry	Leachate, Loading Level (conditions: 250°F, 7 days)	Phenolics Concentrations (mg/L or ppm)
1	Uncured resin (Novolac 1), 3.5g/100 ml DI water	1550
2	Uncured resin (Novolac 2), 3.5g/100 ml DI water	1570
3	Uncured resin (Novolac 2), 30g/100 ml DI water	4390
4	Uncured resin (Novolac 1), 30g/100 ml DI water	4600
5	Uncured resin (Novolac 3), 30g/100 ml DI water	3440
6	Hexa-Cured Novolac 1, 30g/100 ml DI water	21
7	Hexa-Cured Novolac 1, 3.5g/100 ml pH 3 solution	<1*
8	Hexa-Cured Novolac 1, 3.5g/100 ml pH 7 solution	<1*
9	Hexa-Cured Novolac 1, 3.5g/100 ml pH 10 solution	<1*
10	RCP-C (Curable), 100g/100 ml pH 3 solution	<1*
11	RCP-C (Curable), 100g/100 ml pH 7 solution	<1*
12	RCP-C (Curable), 100g/100 ml pH 10 solution	<1*
13	RCP-PC (Pre-Cured), 100g/100 ml pH 3 solution	<1*
14	RCP-PC (Pre-Cured), 100g/100 ml pH 7 solution	<1*
15	RCP-PC (Pre-Cured), 100g/100 ml pH 10 solution	<1*

* **Below Detectable Limits.**

Analytes from Various Leachates and Phenol Standards in UV Cuvettes for Spectrophotometric Measurements



- Narrow calibration range involving phenol standards.
- Samples with high concentrations were diluted with DI water till within the calibrated range, then back-calculated for results.
- Samples with very dilute species made direct use of the original leached solution.

Summary of RCP Leaching Studies

- Two production Novolac RCP Samples, RCP-Pre-Cured (PC) and RCP-Curable (C) were subjected to leaching studies in acidic, neutral, and basic media at elevated temperatures over a week.
- Novolac RCPs were evaluated with regard to finished product performance as well as from an EHS and regulatory perspective via these leaching studies.
- Identification and quantification of these aqueous leachate components were accomplished using proton NMR spectroscopy with water suppression techniques.
- Leachates from both RCP-PC and RCP-C mainly contained formic acid; low concentrations of resin aromatics were observed pointing to very low levels of phenolics in the leachates.
- No free formaldehyde or its hydrated form was detected in the leachates up to the limits of the NMR instrument.
- Leachate analysis specific to free phenol and other phenolics were performed using a standard colorimetric protocol in UV-Vis Spectrophotometry.
- Phenolics (including free phenol) concentrations in these leachates were found to be below the detection capability of the technique (< 1 ppm) based on a standard phenol calibration plot used in the methodology.

ACKNOWLEDGEMENT

- Fairmount Santrol Sustainable Development (SD) and Environmentally Responsible Products and Processes (ERPP) Initiative.

- Dr. Moustafa Aboushabana (Fairmount Santrol Technology Center) for insightful discussions with regard to spectrophotometric analysis of the leachates.

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