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Laboratory Scale Nitration of Cellulose as a Cost Effective Risk Mitigation Tool for the Production of Nitrocellulose at Radford Army Ammunition Plant

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OUTLINE

NITROCELLULOSE MANUFACTURING AT RFAAP

LAB SCALE NITRATION / STABILIZATION

PART I: LAB SCALE NITRATION STUDY

- MIXED ACID COMPOSITION
- KEY INPUT VARIABLES – EFFECTS

PART II: CELLULOSE SOURCE STUDY

- KRAFT VS SULFITE PULP
- ACADEMIC WORK

NITROCELLULOSE MFG. 101

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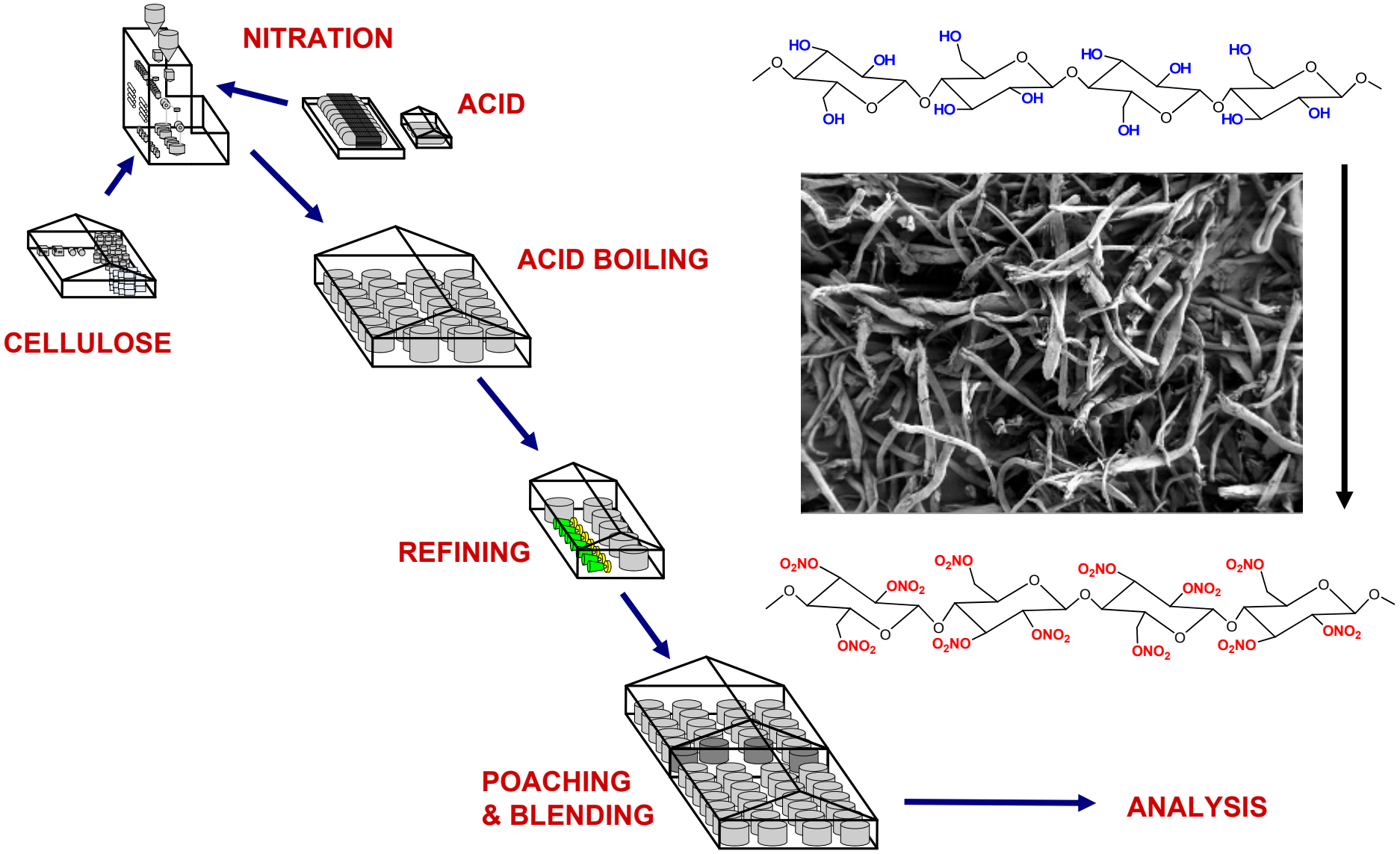

LABSCALE NITRATION

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NITRATION

CELLULOSE

ACID BOILING

REFINING

POACHING

1. **Demonstrate that laboratory nitration can be used as a tool to aid production with risk mitigation associated with sensitive products**

2. **Understand how mixed acid composition and key process input variables (KPIV) change our nitrocellulose in terms of:**

- % Average Nitrogen
- Acetone solubility, and Ether / Alcohol Solubility
- Processing of NC

Grade D Water Sensitivity Models

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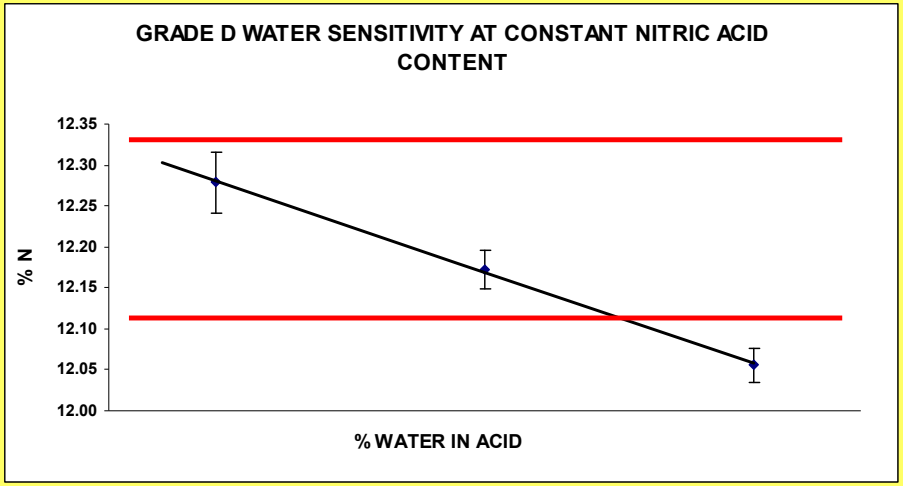
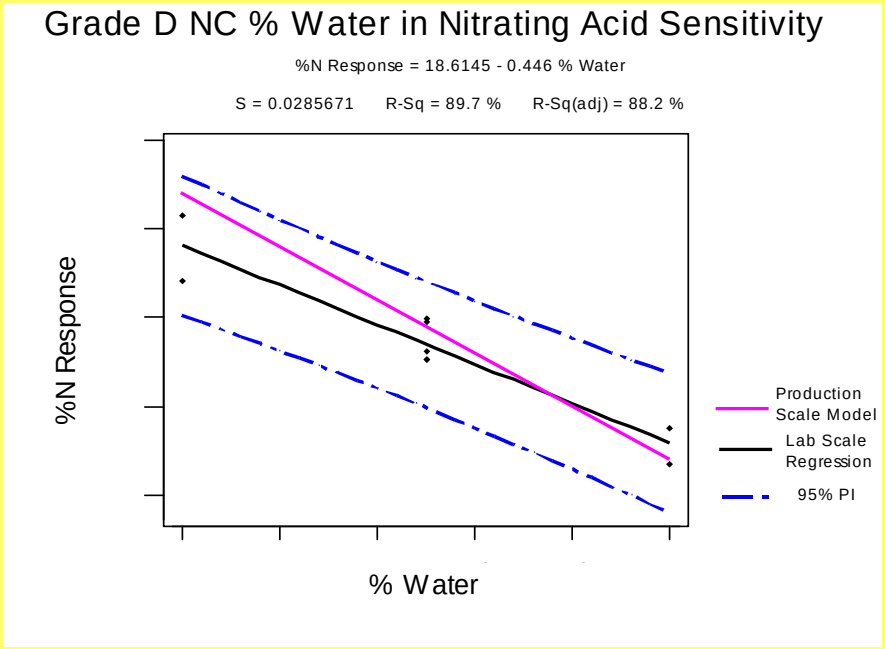
Water sensitivity models developed for Grade D and E nitrocellulose products



Lab data shows linear response of %N to water at current process acid composition

Good fit of data to simple model



AFY09 NC production data fits within lab scale model's 95% prediction limits for Grade D NC

Process data fits have led the NC technical team to use less water set changes during manufacturing

Nitration with various mixed acids

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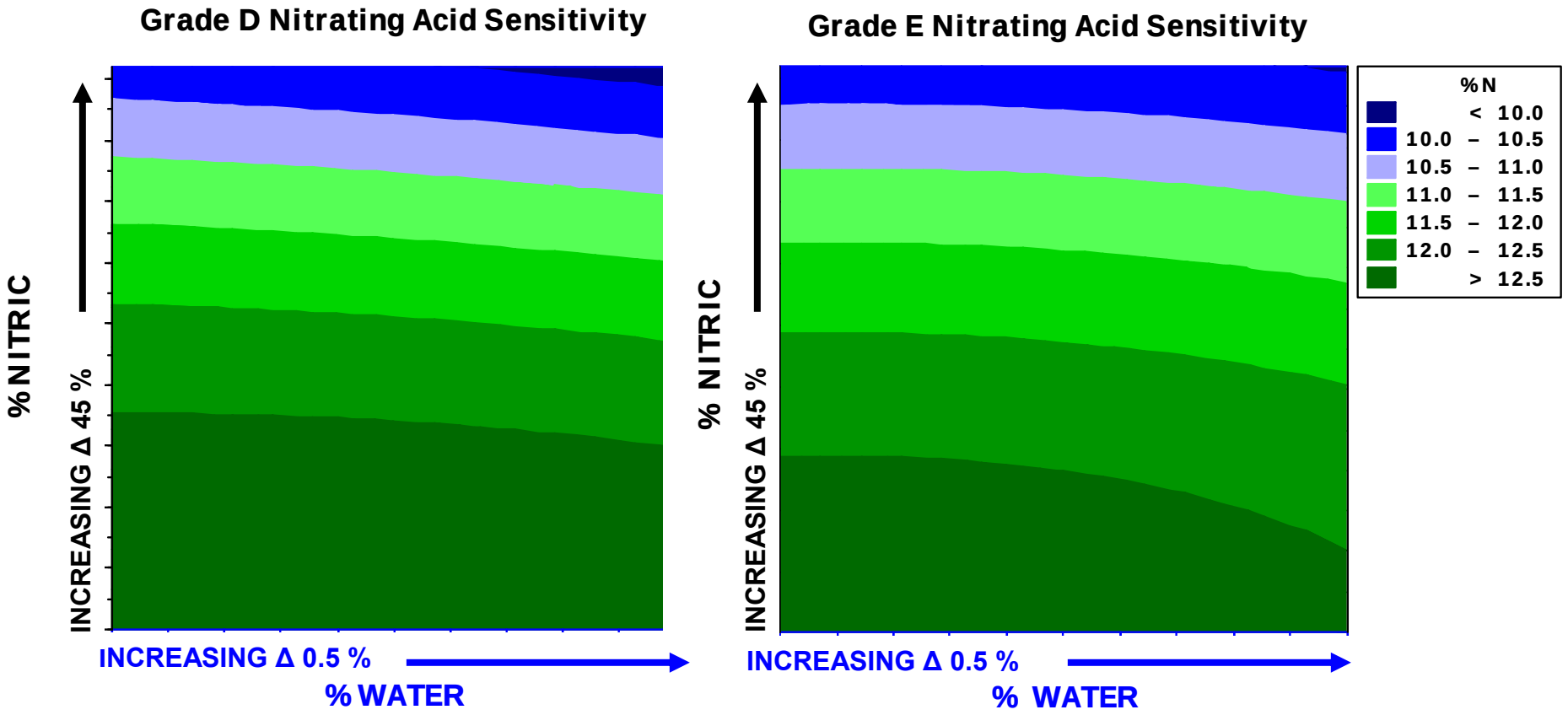

PRODUCTION IS CURRENTLY USING THE MODELS DEVELOPED IN THE LAB TO ADJUST NITRATING ACIDS FOR PRODUCTION OF GRADES D AND E NITROCELLULOSE

KEY PROCESS INPUT VARIABLES AFFECTING ATK NC

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Run	Time (min)	Temp (ºC)	A/C Ratio	Cellulose	%N	AI	EA %Sol	%N	AI	EA %Sol
					GRADE E			GRADE D		
1	HIGH	LOW	HIGH	Chips	**12.051**	0.21	99.70	**12.315**	0.93	98.93
2	HIGH	HIGH	HIGH	Fibers	**12.038**	0.19	99.71	**12.251**	0.59	98.28
3	MID	MID	MID	Fibers	**11.740**	0.59	98.70	**12.182**	0.22	99.18
4	LOW	HIGH	LOW	Fibers	**11.740**	0.91	97.78	**12.040**	1.16	97.57
5	HIGH	HIGH	LOW	Chips	**11.819**	0.10	99.94	**12.105**	0.07	99.66
6	HIGH	LOW	LOW	Chips	**11.804**	2.30	97.78	**12.038**	4.15	95.46
7	LOW	HIGH	HIGH	Chips	**12.043**	1.14	98.65	**12.371**	0.93	99.14
8	LOW	LOW	HIGH	Fibers	**11.809**	1.93	93.71	**12.235**	2.50	93.72
9	LOW	LOW	LOW	Chips	**11.714**	15.68	79.66	**11.865**	11.94	86.92
10	MID	MID	MID	Chips	**11.985**	0.26	99.74	**12.306**	0.14	99.80

VARIABLE (NITRATING ACID MAKEUP FIXED)	RESPONSE		
	AI	EAS	%N
ACID \ CELLULOSE ↑	↓	↑	↑
TEMP. ↑	↓	↑	—
TIME ↑	↓	↑	↑
CHIPS OVER FIBERS	↓	↑	↑

PART II: CELLULOSE SOURCE STUDY

Answer two Questions:

1. **Is it feasible to make nitrocellulose from Kraft paper? Which pulp candidates look most promising?**

2. **Why do similar pulps nitrate so differently? What are the key cellulose characteristics influencing nitration?**

- Hemicelluloses content
- Crystallinity
- Fiber wall thickness
- Tree species used
- Sheet Physical Properties

TWO MAJOR PULPING PROCESSES

SULFATE (KRAFT)

- Basic digestion
- Universal process for recovery of cooking chemicals
- Dominant process
- Cost ~ $ - 0.20 / lb
- Use most types of trees

SULFITE

- Acidic digestion
- Limited recovery of acid gas
- Mills diminishing
- Cost ~ $baseline
- Use limited tree species

NITRATION QUALITY AND SOLUBILITY

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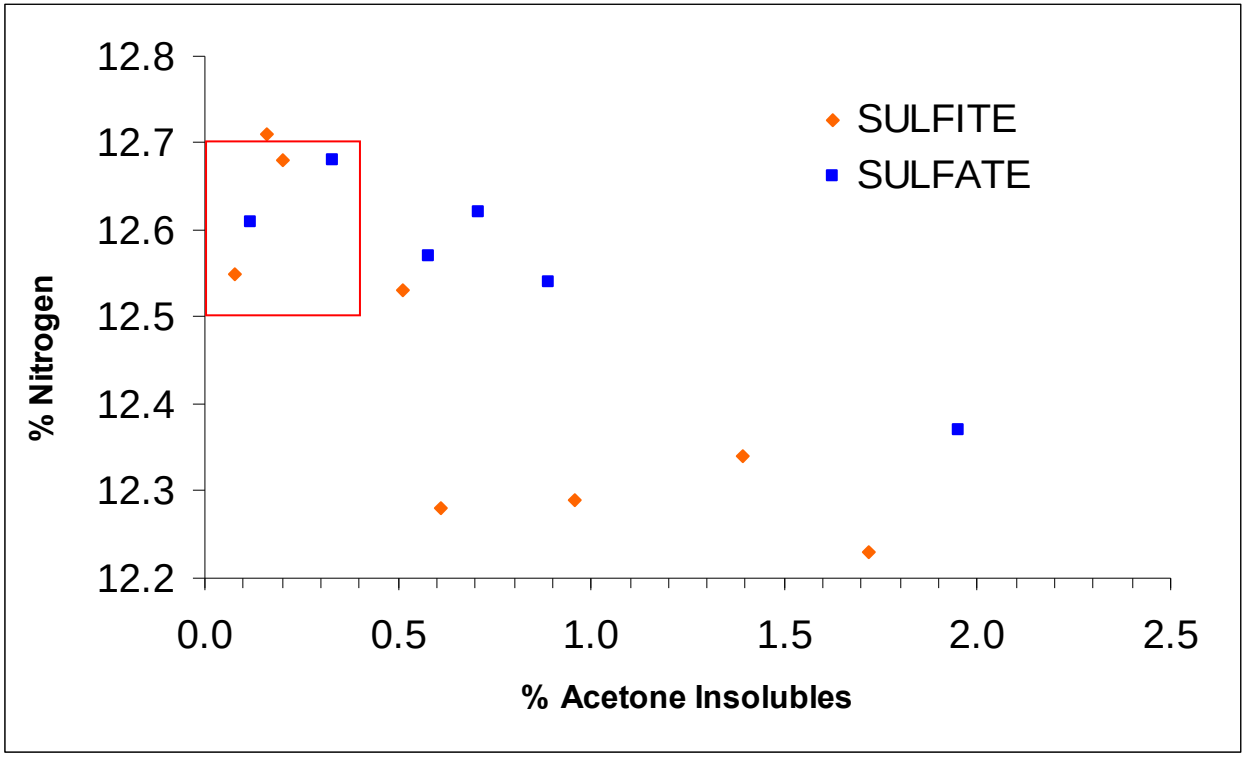
% NITROGEN = 12.6 ± 0.1% , ACETONE INSOLUBLES < 0.4%

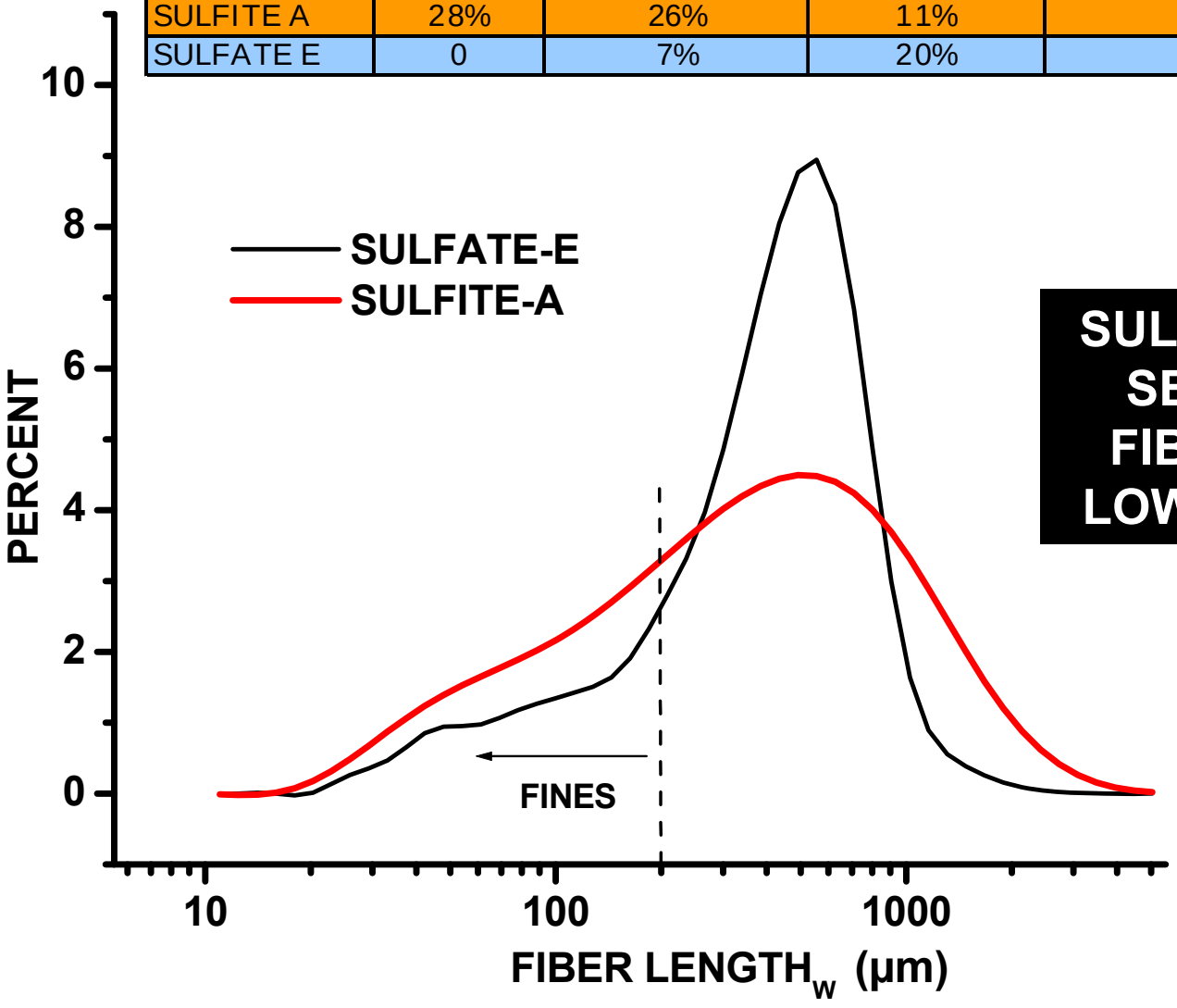


	%N ($FeSO_4$)	%Al	%EAS
SULFITE A	12.68	0.2	99.8
SULFITE B	12.28	0.6	98.9
SULFITE C	12.23	1.7	97.1
SULFITE D	12.53	0.5	99.3
SULFITE E	12.55	0.1	99.9
SULFITE F	12.29	1.0	98.4
SULFITE G	12.71	0.2	99.9
SULFITE H	12.34	1.4	97.9
SULFATE A	12.57	0.6	99.3
SULFATE B	12.62	0.7	99.1
SULFATE C	12.37	2.0	97.5
SULFATE D	12.54	0.9	98.9
SULFATE E	12.61	0.1	99.8
SULFATE F	12.68	0.3	99.8

SEVERAL OF THE SULFATE PULPS TESTED TO DATE APPEAR TO HAVE PROPERTIES THAT MEET MILITARY GRADE NC SPECS

FIBER QUALITY

	PARTICLES			FREE FIBERS
SAMPLE	>850 um	500 - 849 um	250 - 499 um	FINES < 200um
SULFITE A	28%	26%	11%	31%
SULFATE E	0	7%	20%	18%



SULFATE-E IS EASILY SEPARATED INTO FIBERS AND HAS A LOW PERCENT FINES

WOOD PULP FIBERS

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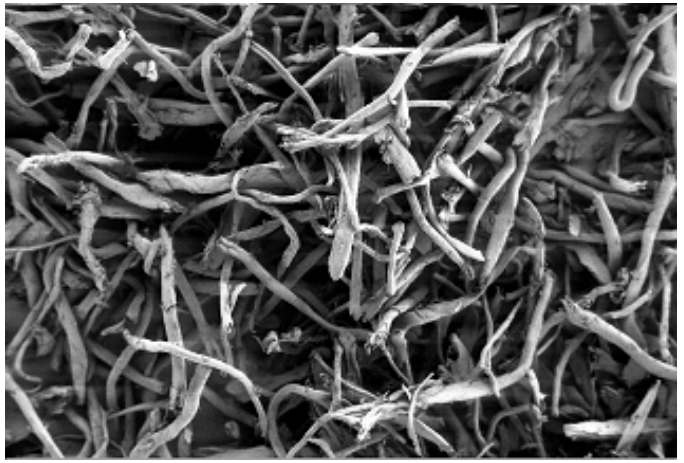
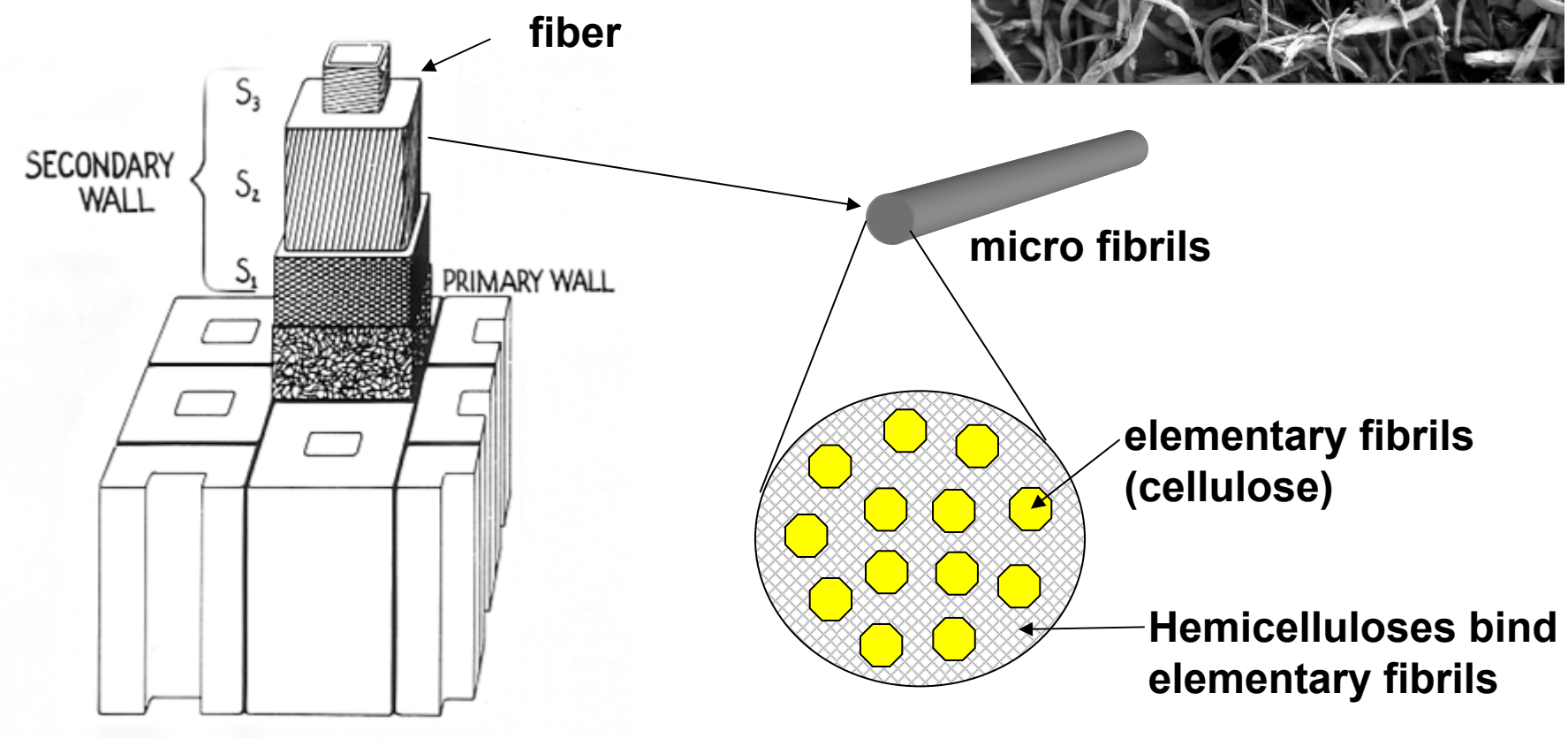
Resin (Extractable) – can survive the pulping process

Lignin – (binder) likely removed during the pulping process

Hemicelluloses (polysaccharides) – can survive pulping process

Alpha Cellulose – survives pulping process





CRYSTALLINITY % AND HEMICELLULOSE %

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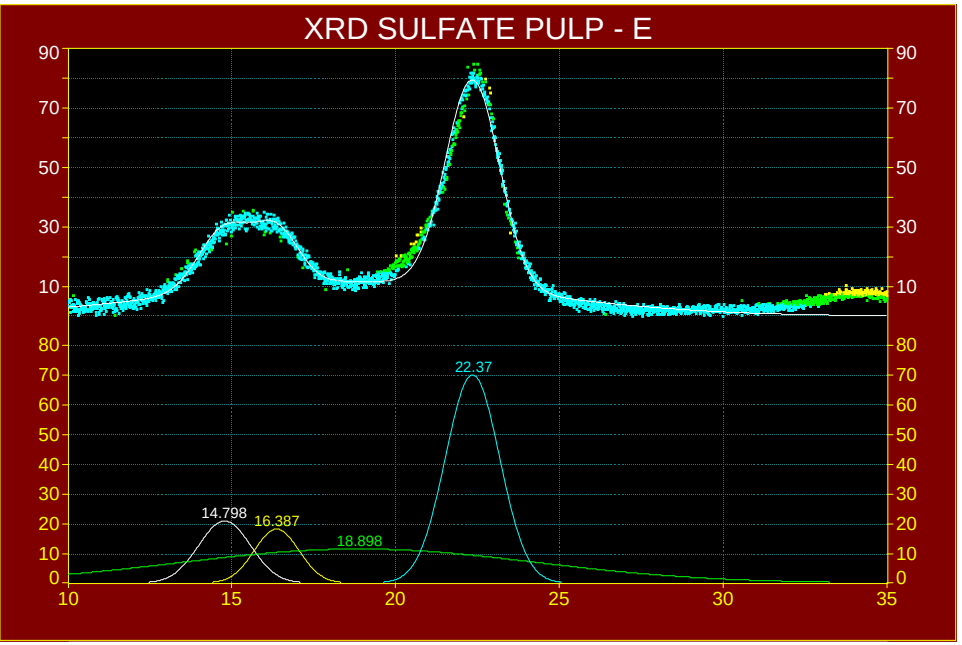

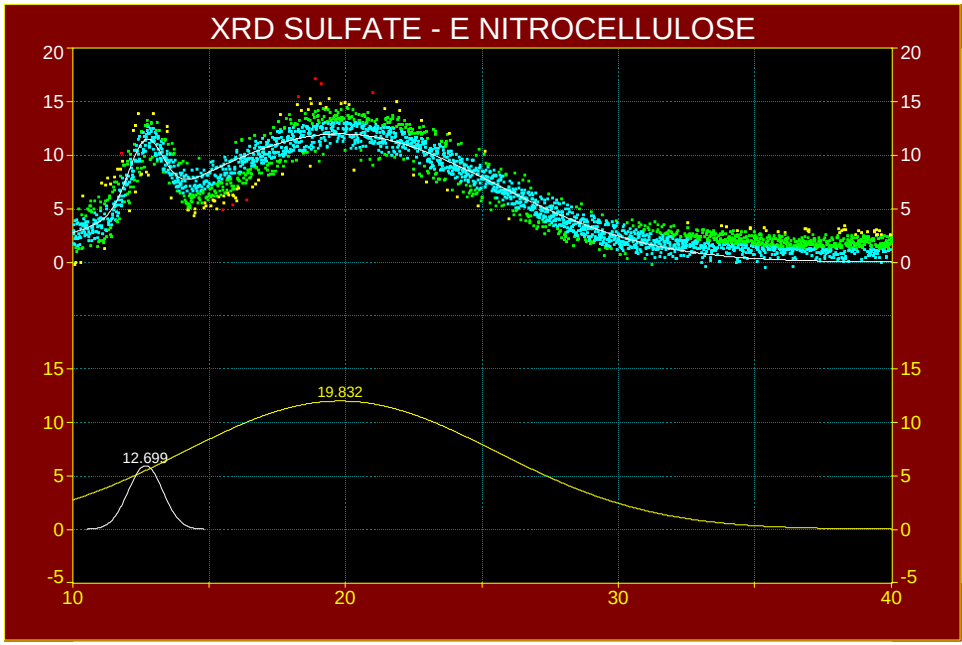

60% CRYSTALLINITY

5% CRYSTALLINITY

SULFITE PULPS	SULFATE PULPS
AVG HEMICELLULOSES = 5%	AVG HEMICELLULOSES = 19%

NEITHER CRYSTALLINITY OR HEMICELLULOSES CONTENT APPEAR TO BE MAJOR FACTORS IN THE NITRATABILITY OF CELLULOSE

CONFOCAL RAMAN MICROSCOPY

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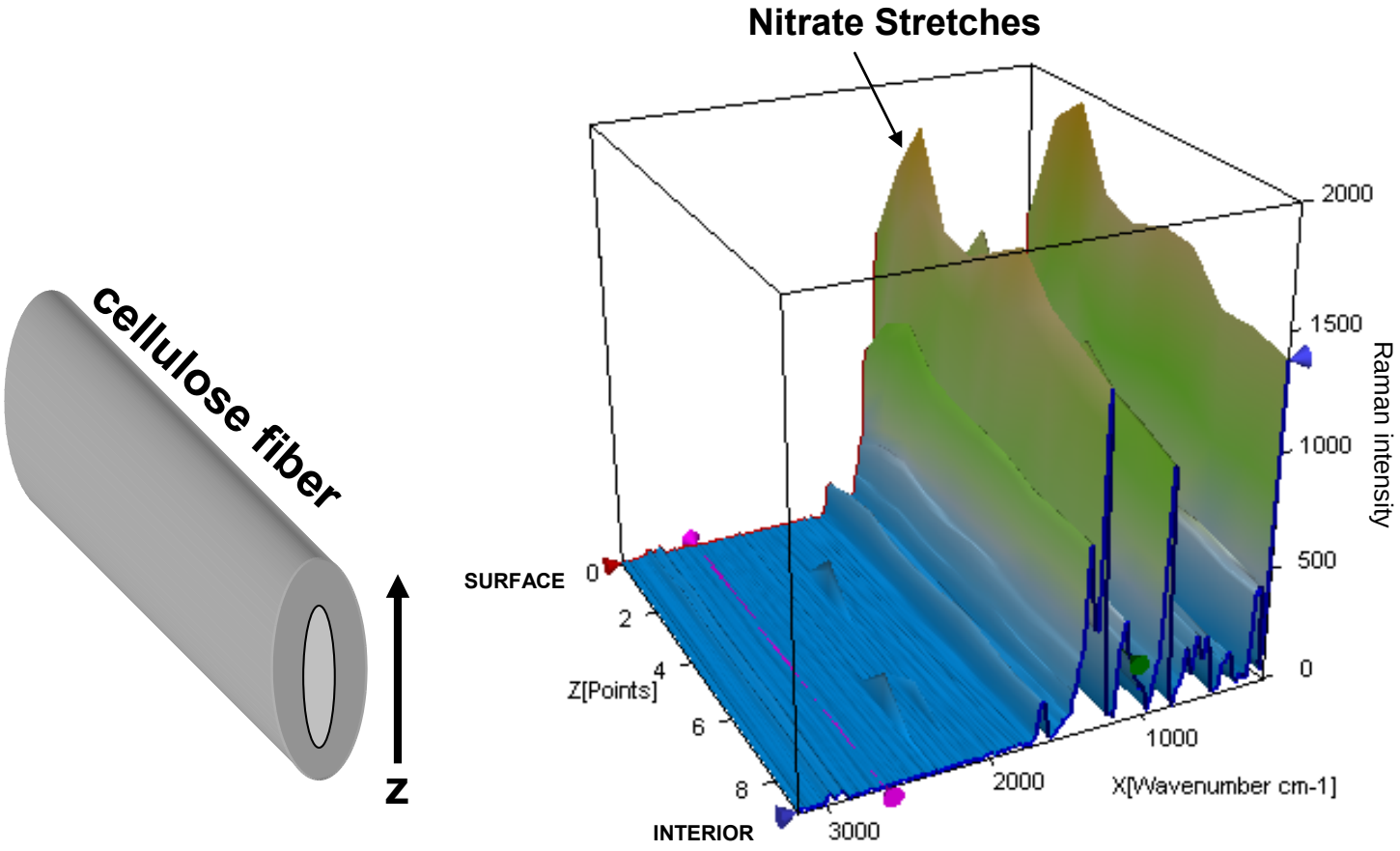

WE ARE COMPARING THE NITRATION LEVEL AT DIFFERENT DEPTHS WITHIN THE FIBER WALL FOR DIFFERENT PULP SAMPLES

CONCLUSIONS

- **WE HAVE BEEN ABLE TO PERFORM NITRATION EXPERIMENTS AT THE LAB SCALE WHICH WOULD HAVE BEEN DIFFICULT, TIME CONSUMING, AND EXTREMELY EXPENSIVE AT THE PRODUCTION SCALE.**

- **LAB SCALE NITRATION HAS BEEN AN EFFECTIVE METHOD FOR TUNING NITRATION CONDITIONS FOR THE PRODUCTION SCALE PROCESS.**

- **LAB SCALE NITRATION IS HELPING ATK TO ASSESS FUTURE SOURCES OF CELLULOSE FOR NC PRODUCTION AS WELL AS ANSWERING SOME FUNDAMENTAL QUESTIONS .**

ACKNOWLEGMENTS

We would like to thank PM Joint Services and ARDEC for funding the cellulose source study portion of this research.