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A Response Surface Methodology (RSM) approach to WC-Co recycling by selective Co dissolution in acetic acid

A. Magumise[1,2,3] S. Ndlovu[1,2] and N. Sacks[1,3]

1. School of Chemical and Metallurgical Engineering, University of the Witwatersrand, Johannesburg, South Africa
2. DST/NRF SARChI: Hydrometallurgy and Sustainable Development; University of the Witwatersrand, Johannesburg, South Africa
3. DST-NRF Centre of Excellence in Strong Materials, South Africa

Introduction

WC-Co scrap

- Sintered products of tungsten carbide (WC) and an iron group metal binder

Straight grades
- WC and Co

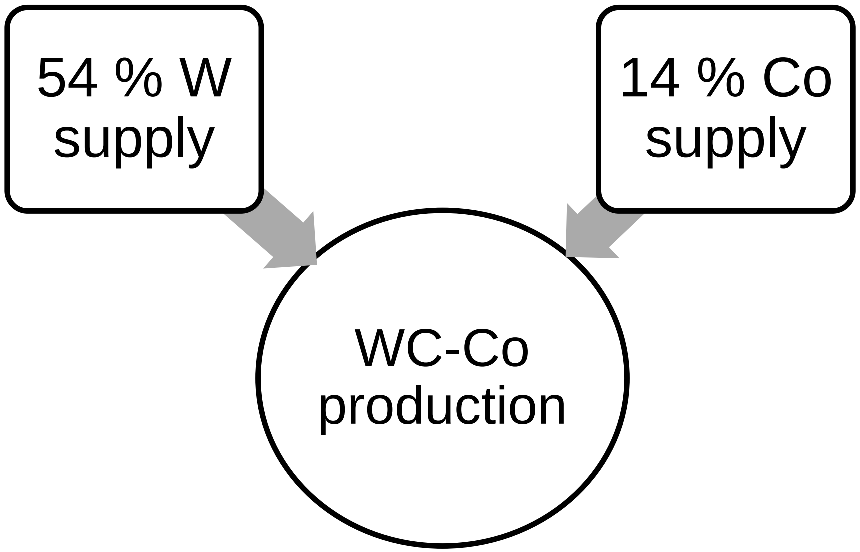
Other grades
- WC , Co and TiC/NbC/TaC

- Additives in minute quantities

WC-Co composition and industrial application

WC %	Co %	TaC %	TiC %	NbC %	Uses
97	3	-	-	-	Precision boring
94	6	-	-	-	General machining
93	7	-	-	-	Cast iron machining
91	9	-	-	-	Cast iron machining
87	13	-	-	-	Wear applications
82	18	-	-	-	Heavy impact uses
80	20	-	-	-	Heavy shock- bar drawing
92.1	5.8	1.8	-	0.3	General machining
74.4	6	7.2	10	2.4	Precision Finishing
79.1	6.7	7	4.9	2.3	Form tooling
75.6	10.7	5.4	6.7	1.6	Interrupted cutting
83.8	13	-	3.2	-	Dies, heavy stock
82	15	3	-	-	Extrusion dies/ can tooling

Project background



Flow of glabal W and Co resources into WC-Co manufacturing

- W and Co are considered critical metals
- W resources are concentrated in a few regions
- Intermittent supply of Co and volatile prices

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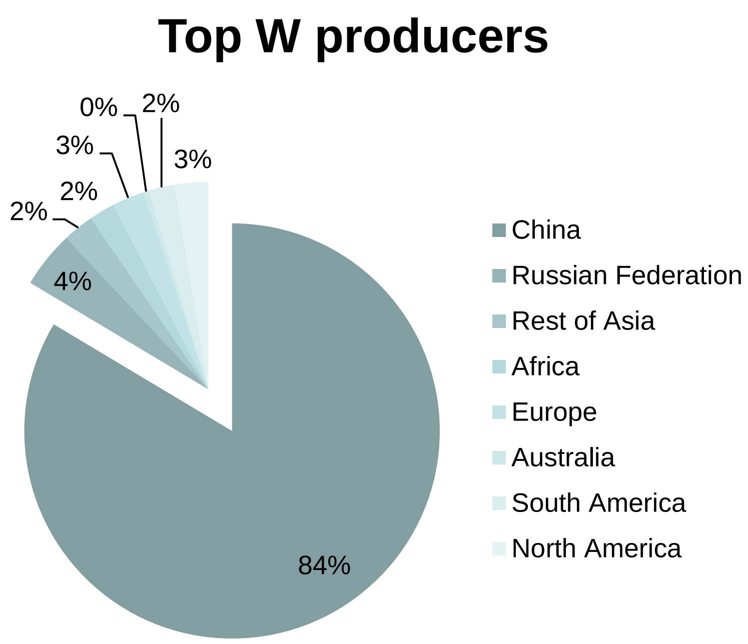
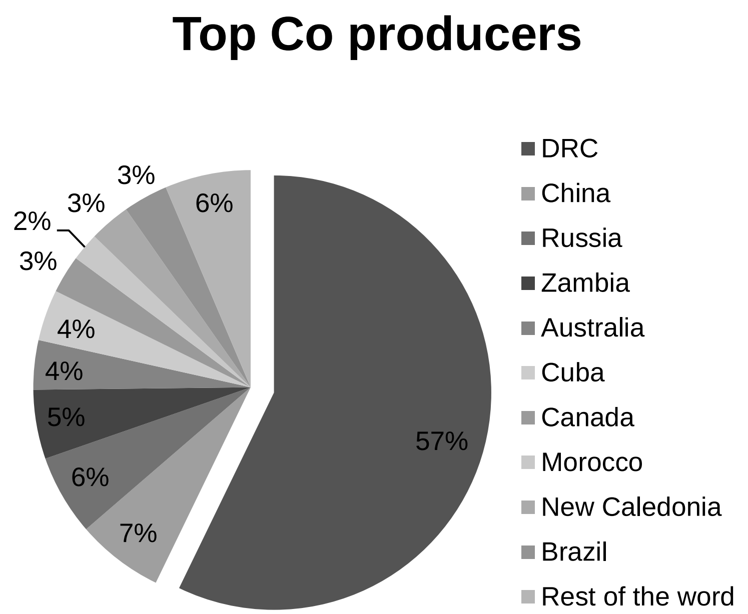
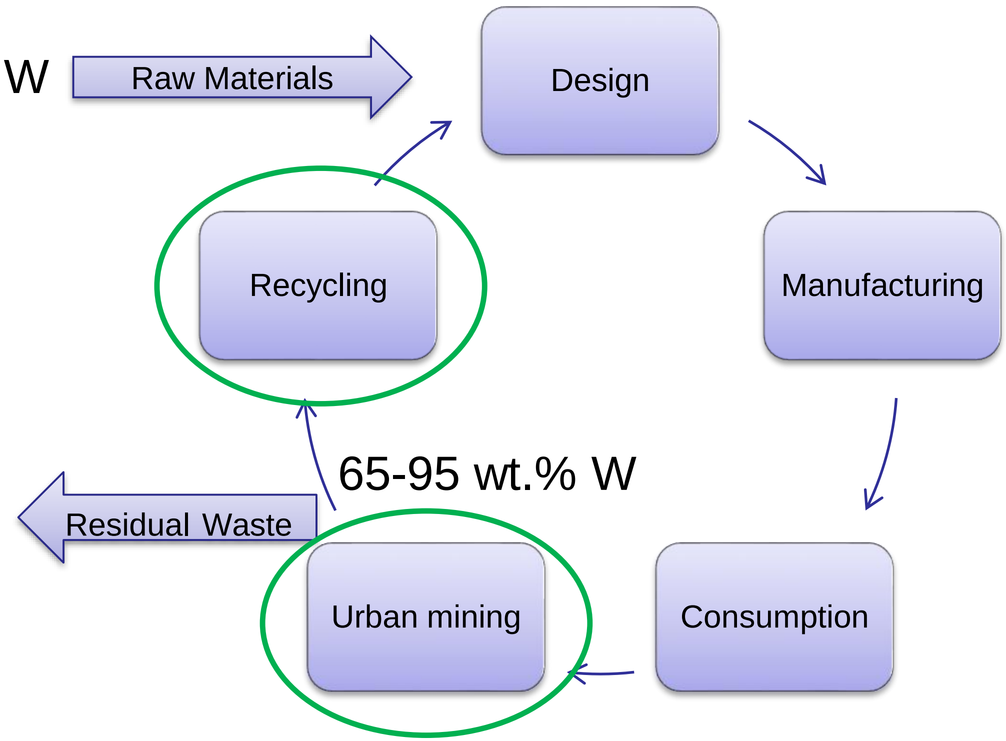
Background





WC-Co Recycling

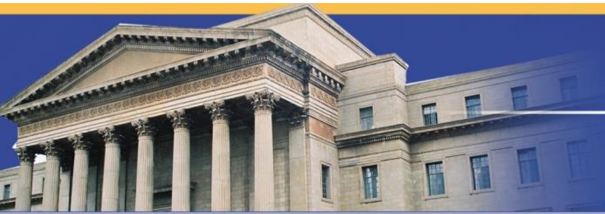
12-60 wt.% W



Why recycle?

Status of recycling

Circular economy



Three categories of WC-Co Recycling

- **Direct Processes**
  - No chemical conversion
  - Zinc Process, Bloating and Crushing
- **Semi-direct processes**
  - Selective Co extraction
  - Chemical dissolution using acids or electrochemical dissolution
- **Indirect processes**
  - Conversion of W and Co to intermediate products
  - Oxidation and subsequent acid or alkali treatment (APT production).

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WC-Co recycling challenges

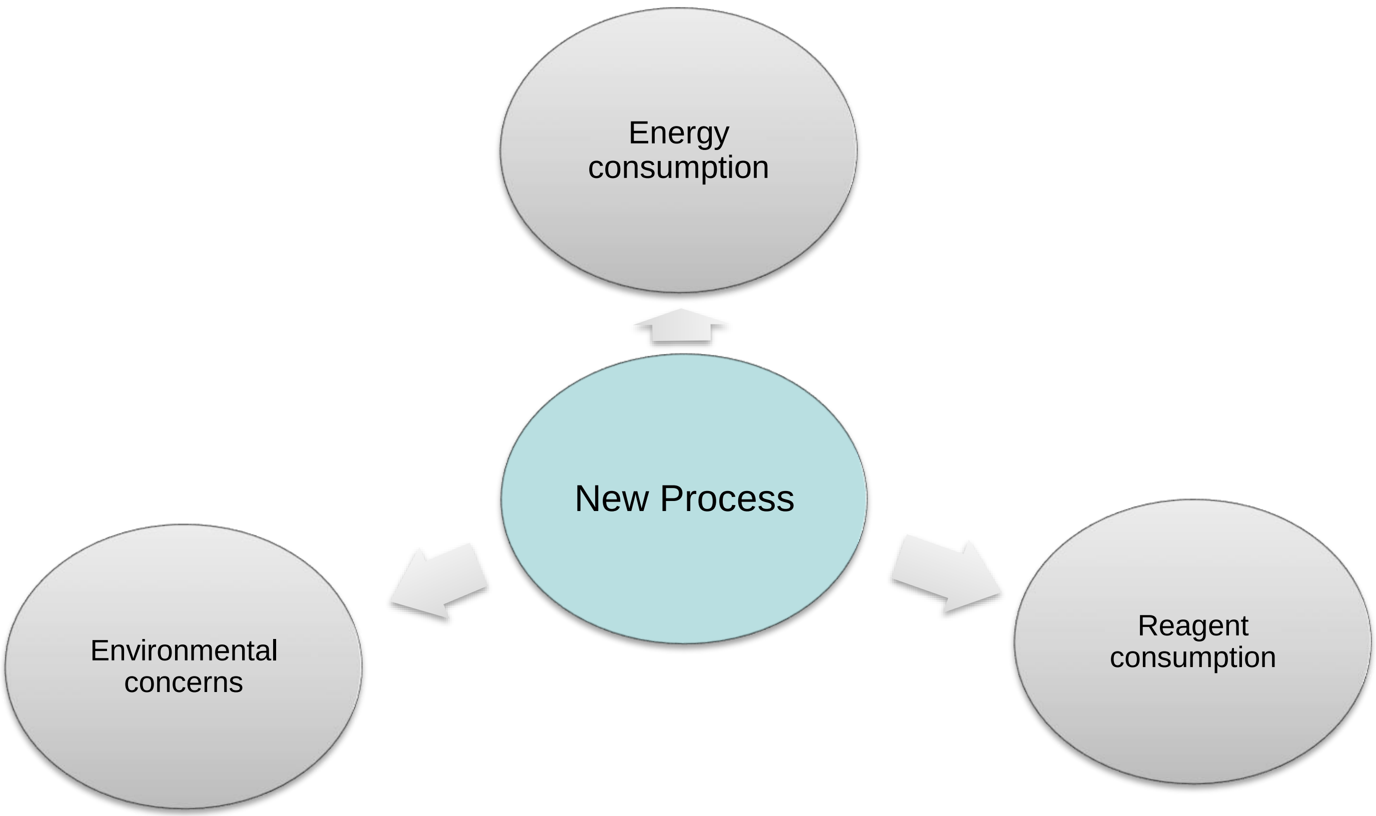
Direct processes:

- Impurity of recycled materials
- Diminished mechanical properties
- High energy consumption (4 000-6 000 kwh/t)
- Poor selectivity

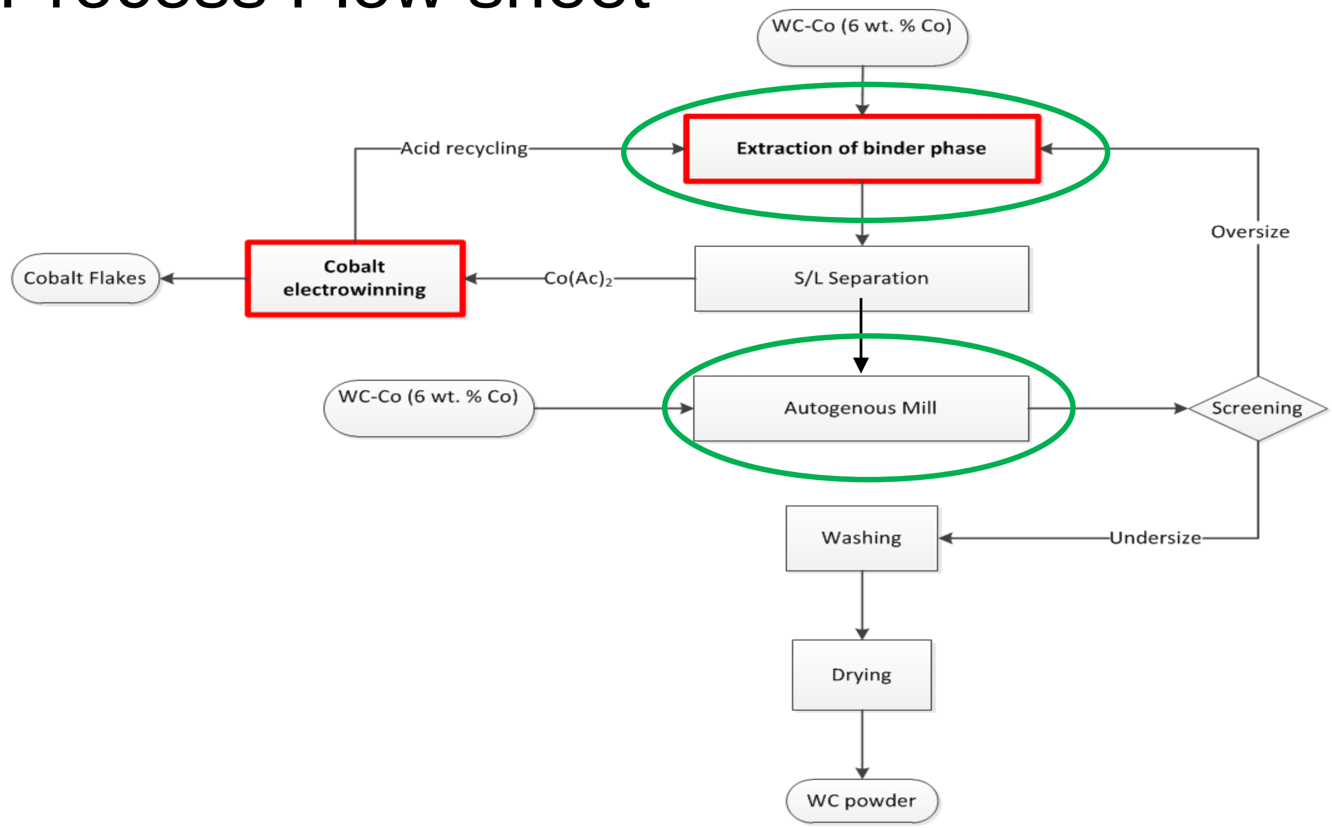
Chemical Processes:

- low recoveries
- High reagent and energy consumption (2 000 kwh/t)
- Lengthy processing times
- Production of toxic effluents and gases associated with use of strong inorganic acids

WC-Co Recycling



Process Flow sheet



WC-Co recycling by selective dissolution of Co using acetic acid followed by microbial electrolytic recovery of Co with simultaneous acid regeneration and wastewater treatment

Leaching and Milling Unit

- A response surface methodology approach for selective Co dissolution from WC-6wt%Co
- Study the effects of concentration, pressure, temperature and ash layer removal on Co dissolution

Co dissolution in acetic acid

- Under oxidising conditions acetic acid selectively dissolves Co:

1. $Co + \frac{1}{2}O_2 + H^+ \rightarrow Co^{2+} + H_2O$ [1]
2. $Co^{2+}(aq) + HAc \leftrightharpoons Co(HAc)^{2+}(aq)$ [2]

Experimental (Equipment)

High pressure autoclave

Benchtop Ball Mill

Experimental (Leaching)

- Solid to liquid ratio 1:16
- Box-Behnken design of experiments:

Parametric discretisation

Parameter	Units		Lower (-1)	Central(0)	Higher (1)
Temperature	° C	X1	40	60	80
Pressure	bar	X2	2	3.5	5
Acid concentration	M	X3	6	10	14

- $Y(Co\ Rec\%) = \beta_0 + \sum_{i=1}^{p} \beta_i X_i + \sum_{i=1}^{p} \beta_{ii} X_i^2 + \sum_{i<j} \sum_{i<j} \beta_{ij} X_i X_j + \varepsilon$ [3]

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Results

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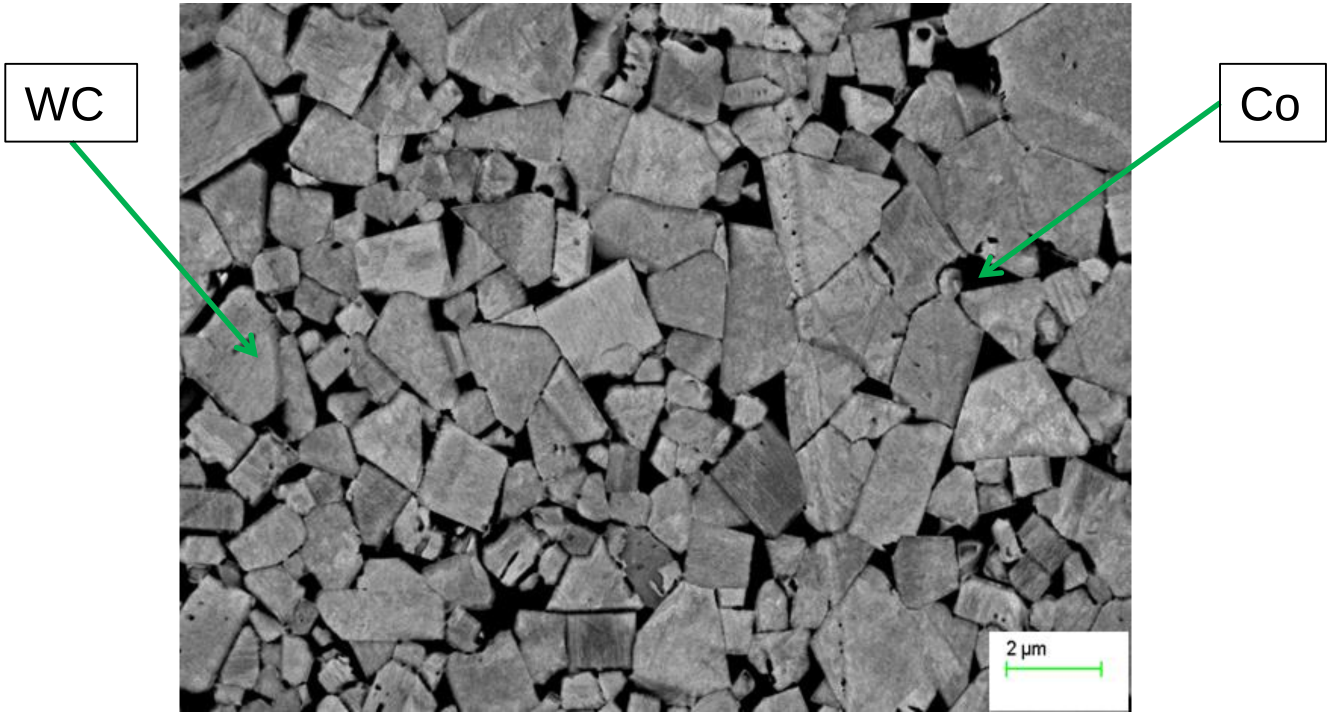
Scrap characterisation



Cross sectional SEM image of WC-6wt.%Co

ANOVA Analysis

- Second order quadratic model for Co recovery % was obtained:

$$\%\,\mathrm{Rec} = 6.2526 - 0.5361\mathrm{T} + 11.9717\mathrm{P} + 0.7831\mathrm{C} + 0.0109\mathrm{T}^2 - 0.1350\mathrm{P}^2 - 0.0277\mathrm{C}^2 - 0.0818\mathrm{TP} - 0.0151\mathrm{TC} - 0.4537\mathrm{PC} \quad [4]$$

S= 1.469 **R^2 = 99.11%** **$R^2_{(adj)}$ = 97.64%**

- Model terms with p-values < 0.05 are considered as significant:
  - Linear terms: **P**
  - Quadratic terms: **T^2**
  - Interaction terms: **PC and PT**

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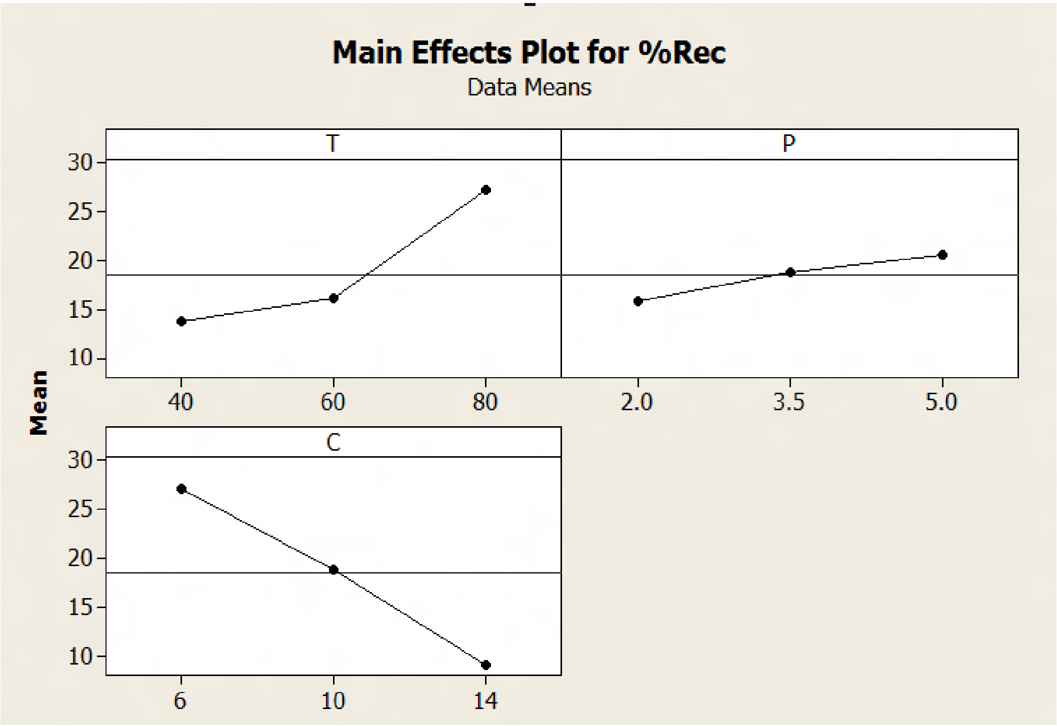
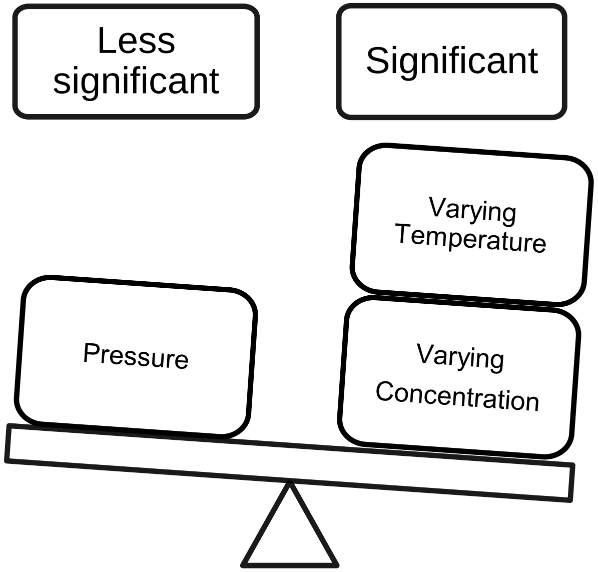
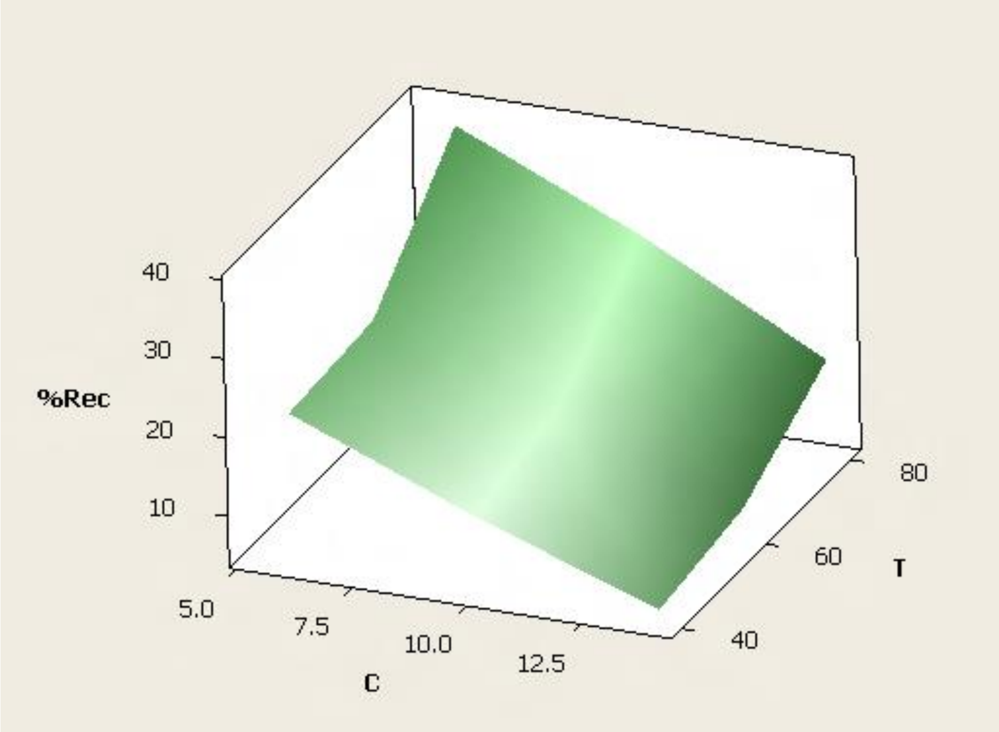
Main Effects Plot





Main Effects Plot

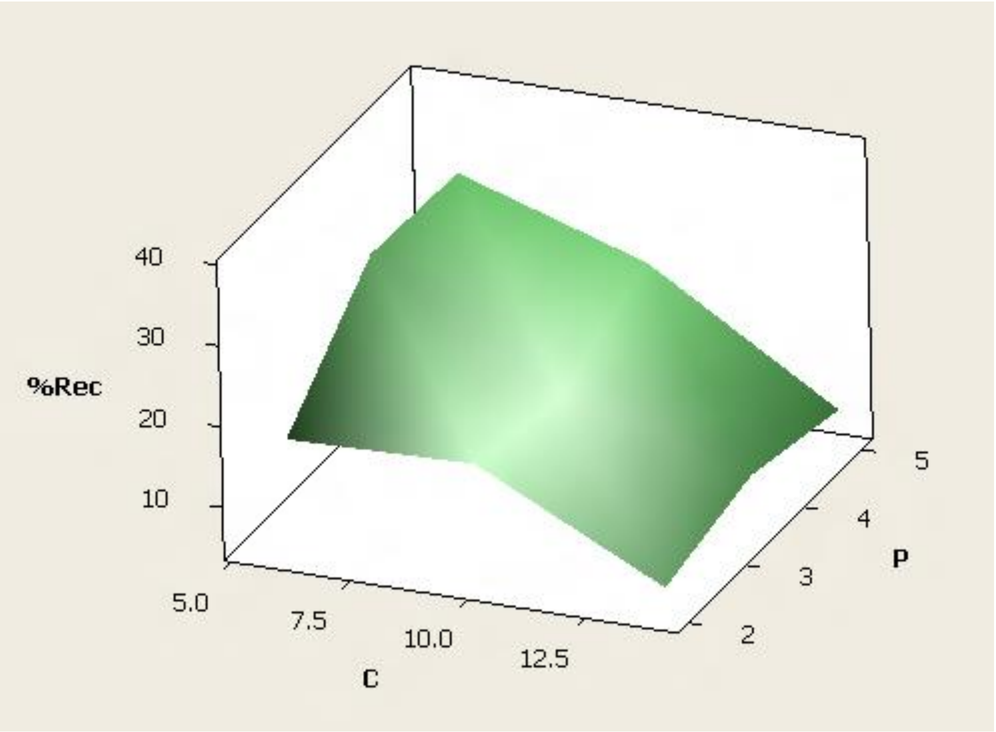
% Rec vs. T,C



- High Co recovery at low acid concentration and high temperatures
- Low pH formation of H_2WO_4

Second order 3-D function for recovery as a function of temperature and concentration

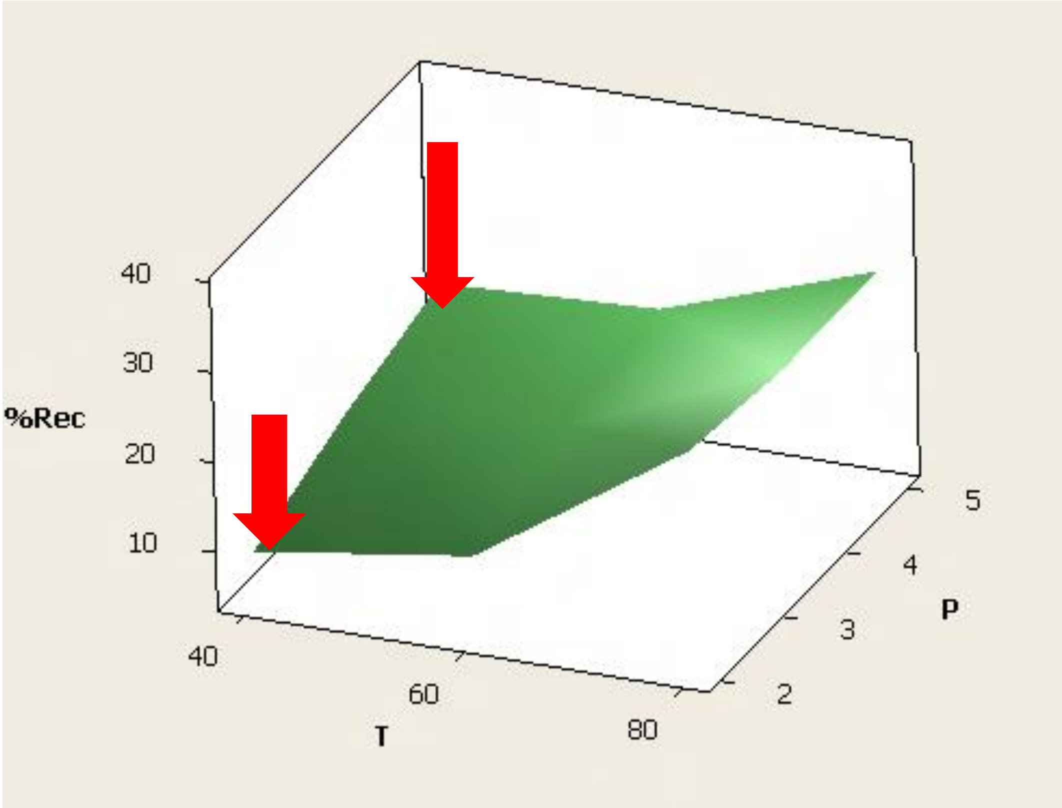
%Rec vs. P,C



Second order 3-D function for recovery as a function of pressure and concentration

- High recoveries at high pressures and low concentration
- High pressures increase O_2 solubility
- Low concentration deter passive film formation

%Rec vs. P,T



Second order 3-D function for recovery as a function of temperature and concentration

- High Co recoveries at high temperature
- Pressure significant at low temperature
- Interaction effect
  O_2 solubility decreasing with increasing temperature

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Discussion

- 38.01 % recovery at 80 C 3.5 bar and 6 M
- Optimal parameters from DoE

T (°C)	P (bar)	C (M)	% Rec
80	5	6	40

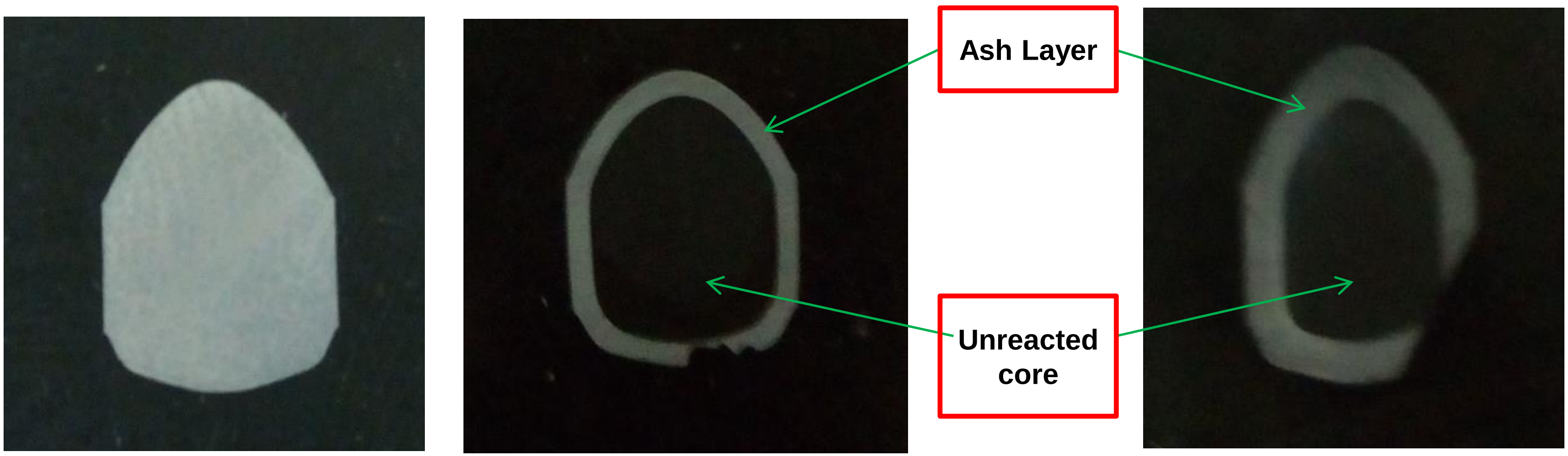
  - 32 % cobalt recovery in 24 hours from scrap containing 8.5wt%Co, 72 wt%. WC, 8 wt%TiC, 11.5 wt%TaC by pressure leaching in phosphoric acid under oxidising conditions (Shwayder, 1969)
  - 40 % cobalt recovery from oxidised WC-Co scrap in 24 hours by leaching in malic acid with H_2O_2 (Seo & Kim, 2016)

Successive Leaching

% Co Recovery with successive leaching

	Run 2 80 °C; 3.5 bar; 6M	Run 6 60 °C;5 bar;6 M	Run 8 60 °C; 2 bar; 6 M
24 h	38.01	29.76	18.28
48 h	28.49	22.46	17.14
72 h	38.36		
Total	**72**	**45.54**	**32.39**

Ash layer progression



Fresh scrap | Lo Co extraction | Higher Co extraction

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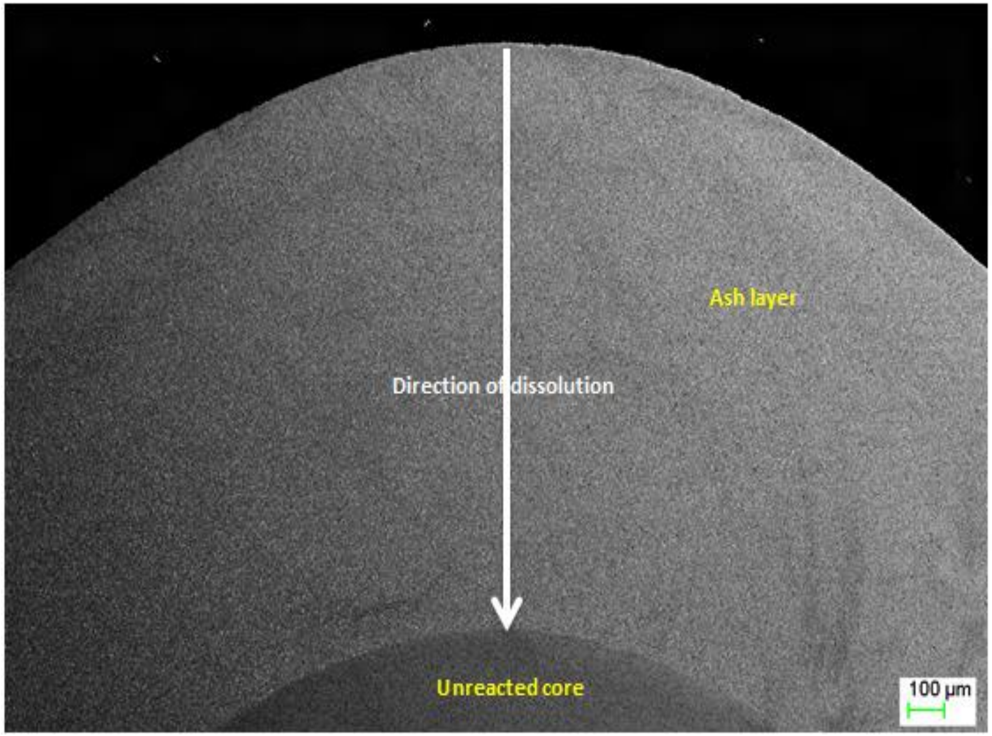
FESM-EDS



SEM image of partially leached insert after 72 % Co recovery

Ash Layer EDS
• W • C • O

Unreacted core EDS
• W • C • Co

Milling Results

- 6 hours milling
- Size reduced from 207 g to 89 g
- Efficiency of cobalt recovery improved to 50 %
- A total of five days for complete Co dissolution

Milling Results

Before milling (207 g)

After milling (89 g)

Recovered Powder FESEM-EDS

SEM image of mill product

- Wide range of particle sizes
- Mill product contamination
- No Co detected

Conclusion

- 80 °C, 5 bar and 6 M were optimal DoE parameters
- Improved Co recovery was observed after milling
- Milling autogenously to avoid mill product contamination
- Integration of the process flow sheet (Microbial Electrolysis Cells
- Performance evaluation of the process
  - Re-sinter WC-Co
  - Economic evaluation
  - Energy balances

Acknowledgments

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science & technology
Department: Science and Technology
REPUBLIC OF SOUTH AFRICA

DST-NRF CENTRE OF EXCELLENCE IN STRONG MATERIALS

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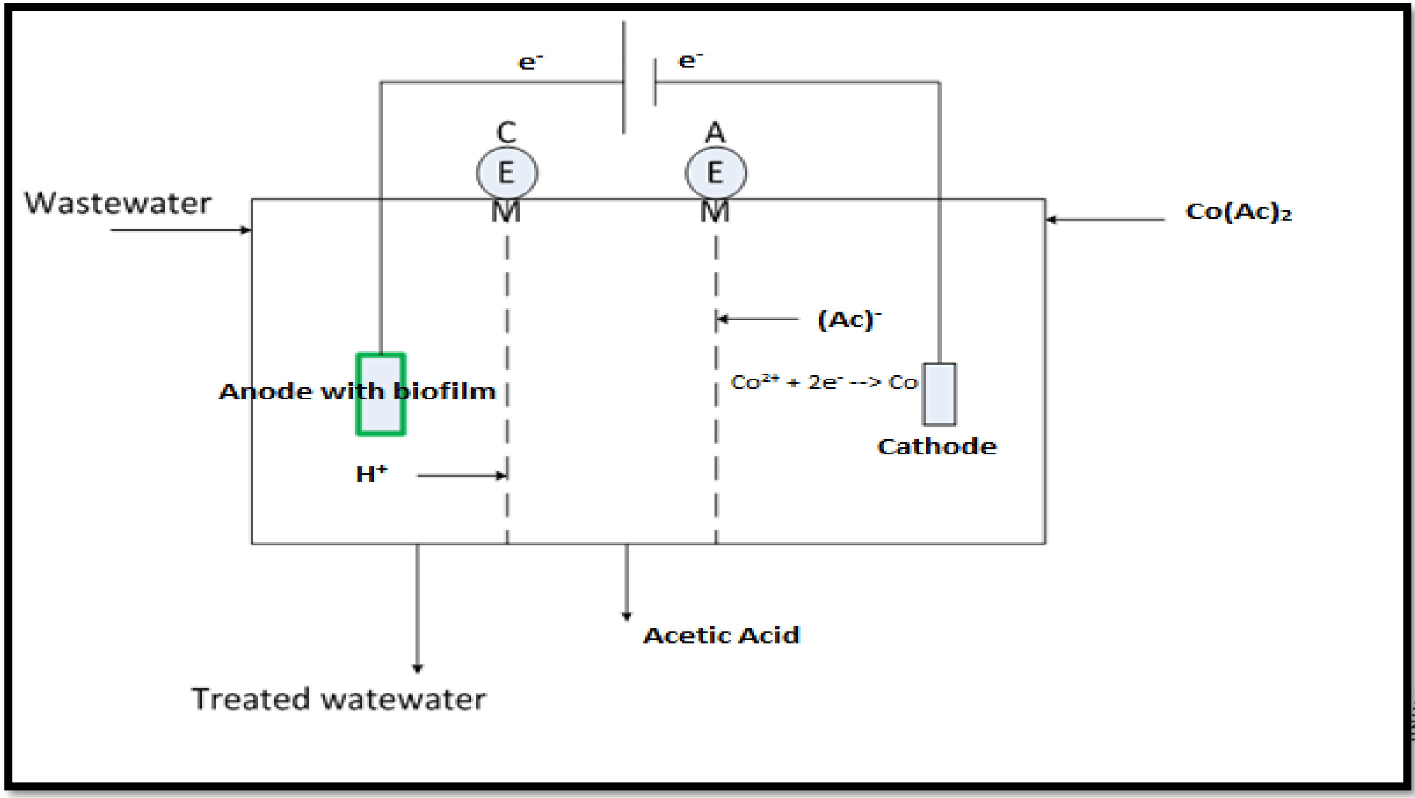
Thank you

Supplementary Slides

Microbial Electro-dialysis cell



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BB DoE

Run	Temperature (°C)	Pressure (Bar)	Concentration (M)
1	40	3.5	14
2	80	3.5	6
3	80	3.5	14
4	40	3.5	6
5	60	2	14
6	60	5	6
7	60	5	14
8	60	2	6
9	40	5	10
10	80	2	10
11	40	2	10
12	80	5	10
13	60	3.5	10
14	60	3.5	10
15	60	3.5	10

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Analysis of variance

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Regression	9	1176.71	1176.71	130.746	65.43	0.000
Linear	3	1038.89	1038.89	346.297	173.30	0.000
T	1	351.79	351.79	351.788	176.04	0.000
P	1	45.03	45.03	45.030	22.53	0.005
C	1	642.07	642.07	642.074	321.31	0.000
Square	3	75.81	75.81	25.269	12.65	0.009
T*T	1	74.35	71.39	71.388	35.72	0.002
P*P	1	0.80	0.91	0.906	0.45	0.531
C*C	1	0.66	0.66	0.660	0.33	0.590
Interaction	3	62.01	62.01	20.671	10.34	0.014
T*P	1	24.11	24.11	24.108	12.06	0.018
T*C	1	8.09	8.09	8.094	4.05	0.100
P*C	1	29.81	29.81	29.812	14.92	0.012
Residual Error	5	9.99	9.99	1.998		
Lack-of-Fit	3	9.97	9.97	3.322	276.11	0.004
Pure Error	2	0.02	0.02	0.012		
Total	14	1186.70				

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Estimated Regression Coefficients for %Rec

Term	Coef	SE Coef	T	P
Constant	6.2526	12.9099	0.484	0.649
T	-0.5361	0.2628	-2.040	0.097
P	11.9717	3.0722	3.897	0.011
C	0.7831	1.1908	0.658	0.540
T*T	0.0109	0.0019	5.713	0.002
P*P	-0.1350	0.3399	-0.397	0.708
C*C	-0.0277	0.0478	-0.580	0.587
T*P	-0.0818	0.0245	-3.341	0.021
T*C	-0.0151	0.0092	-1.647	0.160
P*C	-0.4537	0.1225	-3.706	0.014

- S = 1.41362 PRESS = 159.534
- R-Sq = 99.16% R-Sq(pred) = 86.56% R-Sq(adj) = 97.64%

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