# HEAT ENHANCED HYDROLYSIS OF ENERGETIC COMPOUNDS AND FIELD RESULTS

FORMERLY USED DEFENSE SITE SIOUX ARMY DEPOT, SIDNEY, NE

Molly Maxwell – USACE Emily Crownover - TRS Cindy Crane - HGL April 8, 2020 1:00 p.m. to 3:00 p.m. EDT



### **PROGRAMMATIC APPROACH**

Sioux Army Depot is a Formerly Used Defense Site:

- Property transferred from DOD prior to October 17, 1986
- Responsibility of the US Army Corps of Engineers to evaluate and remediate any residual DOD contamination due to operations at the former facility
- Completed using the CERCLA process
- Congressionally appropriated Defense Environmental Restoration Program (DERP) funds
- Currently in the RI/FS phase



## **TEAMING PARTNERS**

USACE

Program Manager: Molly Maxwell

**Project Manager**: Heidi Durako

#### **Technical Team:**

Geologist - Eric Fritzsch Chemist - Andrea Sansom Risk Assessor – Melanie Karst Engineer – Quang Le



Geologist/Groundwater II: John Flint



**Project Manager:** Chris Williams

Technical Team: Cindy Crane – Lead Engineer Megan Matteazzi – Engineer Joe Vilain – Chemist Kevin Wierengo -Geologist Ken Cottrell – Geologist Lynn Kessler – Program Manager



**Project Manager:** Chris Thomas

**Technical Team:** Emily Crownover – Lead Engineer Brad Morris – Field Construction and Operations Manager James Erario – Project Engineer David Fleming - Founder





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### FORMER SIOUX ARMY DEPOT - LOCATION



- Established by Department of the Army in 1941, built in 1942
- Primary purpose receive, store, and distribute ammunition and ammunition components: included demolition/burning; demilitarization (defusing and removal of propellants & explosives
- Additionally, used to store, service, and distribute other military equipment during and after World War II
- Operations stopped in 1966, transferred in 1967





### SIOUX ARMY DEPOT LAYOUT & TOPOGRAPHY









# **AREA V – AMMUNITION WORKSHOP/RENOVATION AREA**



52 buildings located within this operational area

Most buildings were wooden- decommissioning involved burning and demolition.

4 Leach beds on the designs – 3 were decontaminated by burning

Washout water from the Bomb Washer and Flaker Building 10-1-O was discharged to Leach Bed 10-2-F.





# **GEOLOGY & HYDROGEOLOGY**

Ash Hollow Fm is approximately 150 to 250 feet thick

- predominant materials encountered in all borings were poorly to wellgraded sands, silty clays, silty sands, and clayey silts
- predominant materials encountered at water table depths were sandy clays and silty sands.

Ash Hollow Fm is separated from the underlying Brule Fm of the White River Group by an erosional unconformity

The top of the Brule Fm contains many eroded paleochannels in its surface that are a result of alluvial down cutting

Depth to groundwater is approximately 160 to 165 feet, with flow generally to the East

Average groundwater velocity is 18 feet per year with a horizontal gradient calculated at 0.003 ft per foot. There is essentially no vertical gradient.







### **CONTAMINANTS OF CONCERN**

• Soil (Leach Bed 10-2-F)

#### explosives

TNT (direct contact and leaching) tetryl (direct contact) RDX (direct contact and leaching) 1,3-DNB (leaching 2-amino-4,6-DNT (leaching) 2,6-DNT (leaching)



#### • Groundwater:

explosives 1,3-DNB TNT 2,6-DNT 2-amino-4,6-DNT nitroglycerin PETN RDX tetryl

#### other nitrate and nitrite

metals hexavalent chromium





# **INITIAL PILOT STUDY**

#### Purpose and Objectives

• Evaluate if steam-enhanced alkaline hydrolysis could be considered a viable remedial alternative for the treatment of explosives in soils



Daily readings of temp, pH, ORP and %moisture Soils analyzed by Method 8321A, prep 8330B



- Select 20-foot by 20-foot plot with highest explosives concentrations
- Excavate down to 3 feet and install steam array
- Replace soils
- Mark quadrants (10ft x 10 ft each)
- Collect baseline samples
  - Discrete, 0,1,2 and 5 ft





## ADDITION OF HYDRATED LIME

Soils from the top two feet from each of the four quadrants were then independently:

- 1) Excavated
- 2) Mixed with hydrated lime at a 5% mixture (established through a bench scale test)
- 3) Placed back into their respective quadrants





# SITE MONITORING RESULTS

- Pre pH (7.1) ORP (256 mV) soil temperature (50F) (10C) soil moisture (8-12%)
- Day 1 pH (ranging from 12 to 13) ORP (down to -100 to -150 mV range) soil temperatures (100 -125 F) (37.8-65.6 C) soil moisture (38 to 48% range)



- Day 3 soil pH and ORP levels starting to transition toward pre-treatment conditions pH (10.5 to 12.2 range) ORP (-5 to -36 mV)
- Day 5 soil pH and ORP are essentially at pre-treatment conditions, added alkalinity was completely exhausted
- Day 10 Quadrants 1 & 2 received another 5% alkaline mixture, remixed independently. Quadrant 3 & 4 left undisturbed, continued receiving steam

Day 20 - Steam treatment ends





### RESULTS

		Quadrant 1			Quadrant 2			Quadrant 3			Quadrant 4							
mg/kg	ft bgs	Pre	10 days	20 days	% reduction	Pre	10 days	20 days	% reduction	Pre	10 days	20 days	% reduction	Pre	10 days	20 days	% reduction	Avg % reduction
RDX	0	890 U	250	41	83.6	930	240	160	33.3	890 U	240	140	41.7	890 U	370	11	97.0	
	1	890 U	120	27	77.5	890 U	290	86	70.3	890 U	68	140	-105.9	890 U	370	4.8	98.7	
	2	890 U	140	80	42.9	890 U	240	190	20.8	890 U	340	110	67.6	890 U	140	10	92.9	
	5	890 U	-	12	-	890 U		13	-	890 U	-	29	-	890 U	420	30	-	
	Avg	-	170	40	76.5	-	257	112	56.3	-	216	105	51.5	-	293	14	95.2	69.9
TNT	0	2900	300	22	99.2	4900	390	520	89.4	2100	240	54	97.4	2900	400	45	98.4	
	1	1900	68	2.4	99.9	3300	700	98	97.0	370	18	12	96.8	5500	110	26	99.5	
	2	3300	50	120	96.4	1800	600	180	90.0	1600	1000	9	99.4	3800	960	30	99.2	
	5	160	-	5	96.9	300	-	2.8	99.1	110	-	2.3	97.9	190		8.4	95.6	
	Avg	2065	105	37	98.2	2575	423	200	92.2	1045	315	19	98.2	3098	368	27	99.1	96.9





## CONCLUSIONS

Quadrant-averaged total concentration reductions (relative to pre-treatment concentrations)

- 64 % to 85% after 10 days of treatment
- 86% to 97% after 20 days of treatment

Quadrants 1 and 2 (double dose of 5% lime), concentration reductions were generally similar to or less than those in quadrants 3 and 4, where a single dose of lime (5%) was applied

The 5% lime mixture appears to be insufficient to consistently treat highly concentrated explosive levels (i.e. explosive concentrations ~ 900 mg/kg [900,000 ug/kg] and above) to below both residential and industrial RSLs.

The alkaline conditions resulting from addition of hydrated lime at 5% mixture typically lasted for up to a 3 to 4-day period following each dosage event, transitioning back to ambient conditions thereafter. A higher dose is needed to prolong the effects of hydrolysis.

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Consideration should be given for the use of in-situ thermal treatment (without hydrated lime added) as a remedial alternative for the site





## SO WHAT'S NEXT?

We have some answers for our approach to explosives in the soils within the top 10 feet

But how do we address the deeper soils that are acting as a continuing source for the groundwater?

Generating alkaline conditions to support alkaline hydrolysis has proven to be difficult in situ, and excavation is not a plausible alternative....

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How about heat????







#### HEAT ENHANCED HYDROLYSIS OF ENERGETIC COMPOUNDS AND FIELD RESULTS: ERH FIELD IMPLEMENTATION

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#### HEAT ENHANCED HYDROLYSIS OF ENERGETIC COMPOUNDS



**RDX DEGRADATION PATHWAYS** 





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## IN SITU THERMAL REMEDIATION TECHNOLOGY COMPARISON





### ELECTRICAL RESISTANCE HEATING TECHNOLOGY OVERVIEW





File Name

#### **PILOT AREA ENERGETIC COMPOUND CONCENTRATIONS**







#### ELECTRICAL RESISTANCE HEATING PROCESS DESIGN

# SITE FLYOVER







#### **ELECTRICAL RESISTANCE HEATING SYSTEM**





File Name



#### SITE AVERAGE TEMPERATURE RESPONSE TO ENERGY APPLICATION



File Name

857,737 kWh subsurface energy applied Peak average temperature: 87.4 degrees Celsius Minimal temperature decrease with downtime







### **ENERGY APPLICATION REQUIREMENT EVALUATION**

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Rate of energy (power) input highest during heat-up phase Subsurface rewetting increased heat-up rate Lower power requirement for temperature maintenance Minimal temperature decrease with electrode de-energization Power cycling option for continued temperature maintenance





File Name

## **CONCLUSIONS OF PILOT TEST DESIGN, CONSTRUCTION, & OPERATIONS**

Electrical resistance heating field demonstration implemented for heat enhanced energetic hydrolysis pilot study at Sioux Army Depot

Rewetting system enhanced heat-up rate increasing energy application efficiency

Upon heating up pilot study target treatment volume, reduced rate of energy input required

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Larger scale implementation

- Increased rewetting system distribution to further increase heat-up rate
- Wider electrode spacing to increase energy efficiency
- Power cycling for temperature maintenance over longer duration for further energy efficiencies



File Name

# **QUESTIONS FOR EMILY?**





#### SIOUX ARMY DEPOT AREA V – PILOT STUDY PERFORMANCE

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## PILOT STUDY PERFORMANCE MONITORING

Pilot study sampling plan

- -Sampling frequency
  - Baseline
  - 4 months after start of heating
  - 6 months after start of heating
- -Samples
  - Discrete samples collected near 2 locations sampled during historical investigations
  - 5-point composite samples collected from 4 quadrants
  - At all locations, samples collected at 10 15 ft bgs, 20 25 ft bgs, and 65 70 ft bgs
  - In southwest quadrant, composite sample also collected at 70 75 ft bgs to assess if explosives had leached below the treatment zone
- All samples analyzed for explosives with United States Environmental Protection Agency (USEPA) Method 8330B
- All composite samples extracted with synthetic precipitation leaching procedure (SPLP) and leachate analyzed for explosives with USEPA Method 8330B



### PILOT STUDY PERFORMANCE MONITORING (CONT.)



#### **BASELINE DATA**

Primary contaminants

- -RDX
- -HMX
- -2,4,6-TNT
- -1,3,5-TNB
- -1,3-DNB
- -2,4-DNT and 2,6-DNT
- -2-amino-4,6-DNT and 4-amino-2,6-DNT

Explosives detected in 1 or 2 soil samples

- -PETN
- Tetryl
- -3,5-Dinitroaniline

Explosives not detected in any sample: nitrotoluenes, nitrobenzene, and nitroglycerin



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### **BASELINE RESULTS FOR PRIMARY CONTAMINANTS - SOIL**

Explosive	Detection Frequency	Detection Range (mg/kg)	Average Detection (mg/kg)
RDX	19/19	5.7 - 28	16
НМХ	19/19	0.14 - 15	3.8
2,4,6-TNT	19/19	0.37 - 9.6	3.6
1,3,5-TNB	19/19	0.45 - 31	10
1,3-DNB	14/19	0.041 - 0.28	0.14
2,4-DNT	19/19	0.12 - 3.1	0.96
2,6-DNT	9/19	0.026 - 0.13	0.061
2-amino-4,6-DNT	17/19	0.036 - 0.18	0.11
4-amino-2,6-DNT	7/19	0.037 - 1.2	0.26



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### **BASELINE RESULTS FOR PRIMARY CONTAMINANTS - SPLP**

Explosive	Detection Frequency	Detection Range (ug/L)	Average Detection (ug/L)
RDX	13/13	330 - 1,300	800
нмх	13/13	12 - 750	220
2,4,6-TNT	13/13	10 - 360	150
1,3,5-TNB	13/13	10 - 1,100	310
1,3-DNB	12/13	2.2 - 12	5.9
2,4-DNT	13/13	6.5 - 110	43
2,6-DNT	12/13	0.32 - 3.8	1.6
2-amino-4,6-DNT	8/13	2.2 - 4.9	3.7
4-amino-2,6-DNT	4/13	1.3 - 180	47





# **BASELINE DATA (CONT.)**

Baseline data evaluated using box-and-whisker plots, hypothesis testing, and goodness-of-fit to determine whether to pool the sampled intervals or keep separate for subsequent evaluation of performance data

- RDX, 2,4-DNT, 2-amino-4,6-DNT, and 1,3-DNB baseline concentrations pooled across all sample intervals
- -2,4,6-TNT baseline data for 20 25 ft bgs and 65 75 ft bgs pooled and shallow results (10 15 ft bgs) kept separate
- HMX and 1,3,5-TNB baseline results for 10 15 ft bgs and 20 25 ft bgs pooled and results for 65 75 ft bgs kept separate
- -2,6-DNT and 4-amino-2,6-DNT baseline results pooled due to low detection frequencies within each sampled interval

SPLP leachate concentrations were generally correlated with soil concentration

Exception: 4-amino-2,6-DNT 2 highest baseline leachate concentrations associated with non-detect soil results

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## **PERFORMANCE MONITORING – MONTH 4 DATA**

Substantial decreases in RDX, HMX, 2,4,6-TNT, and 2,4-DNT detections

-RDX

- Soil and SPLP detections decreased at all sample locations
- Not detected in 17 of 19 soil samples (as compared to baseline detection frequency of 19/19)
- Not detected in 11 of 13 SPLP samples (as compared to baseline detection frequency of 13/13)

#### -HMX

- Soil detections decreased at 18 of 19 sample locations
- SPLP detections decreased at 12 of 13 sample locations
- Not detected in 10 of 19 soil samples (as compared to baseline detection frequency of 19/19)
- Not detected in 7 of 13 SPLP samples (as compared to baseline detection frequency of 13/13)

#### -2,4,6-TNT

- Soil detections decreased at 15 of 19 sample locations
- SPLP detections decreased at 12 of 13 sample locations

#### -2,4-DNT

- Soil detections decreased at 17 of 19 sample locations
- SPLP detections decreased at 11 of 13 sample locations

Strong evidence of degradation of the above explosives







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Results for remaining primary contaminants

- -1,3,5-TNB: no consistent change in concentration between baseline event and 4-month event
- -1,3-DNB: all but one location showed an increase or no substantial change in soil concentration
- -2,6-DNT:
  - Difficult to evaluate soil data because many detections similar to or less than the reporting limit
  - SPLP data suggestive of degradation
- -2-amino-4,6-DNT: soil concentration decreased at approximately half of the locations
- -4-amino-2,6-DNT: most locations showed an increase or no substantial change in soil concentration
- -3,5-Dinitroaniline:
  - Substantial increase in soil concentration with detection frequency increasing from 2 of 19 during the baseline event to 18 of 19 at 4 months

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• SPLP leachate concentration increased at all locations



#### RDX

- Detected in only 1 soil sample: 1.2 mg/kg in the northwest quadrant sample from 65 70 ft bgs (baseline detection of 20 mg/kg)
- -Soil detections decreased by  $\geq$  94% at all locations
- Detected in only 1 SPLP sample: 44 ug/L in the same sample with the soil detection (baseline SPLP result of 930 ug/L)
- -SPLP leachate concentrations decreased by  $\geq$  95% at all locations

#### HMX

- -At 18 locations, soil detections decreased between 58% and >99%
- At one location, 65 to 70 ft bgs in northeast quadrant, the 6-month soil detection was 0.98 mg/kg as compared to baseline result of 0.27 mg/kg
- -All SPLP leachate concentrations decreased between 66% and >99%









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#### 2,4,6-TNT

-Soil concentrations at all locations decreased between 86% and >99%

-SPLP leachate concentrations at all locations decreased between 95% and >99%

#### 2,4-DNT

- -Soil concentrations at all locations in treatment zone (10 70 ft bgs) decreased between 56% and 99%
- In 70 75 ft bgs sample, 6-month result was 0.16 mg/kg, slightly less than baseline detection of 0.19 mg/kg but not clear if this is a true decrease in concentration given sampling and analytical variability
- SPLP leachate concentrations at all locations, including the 70 75 ft bgs location, decreased between 31% and >99%

Similar to 4-month data, the 6-month data show strong evidence of RDX, HMX, 2,4,6-TNT, and 2,4-DNT degradation



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#### 2,6-DNT

- -Detected in only 2 of the 19 6-month soil samples. Both detections less than the reporting limit.
- Greater detection frequency in SPLP leachate samples (both baseline and 6-month) as compared to soil samples.
- Hypothesis testing concludes that baseline and 6-month SPLP results are statistically the same, but boxand-whisker plots suggest a decrease in SPLP concentrations during treatment.

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- -At most locations (9 of 13), SPLP result at 6 months was less than baseline.
- -Analytical results suggestive of 2,6-DNT degradation.











#### 4-amino-2,6-DNT

- Detected in one soil sample for the 6-month event. Detection is 92% less than corresponding baseline result. These soil results suggest degradation.
- Detected in 4 of 13 baseline SPLP samples. For these locations, 6-month SPLP results show decreases ranging from 70% to 99%, suggesting degradation.
- –At 9 locations with non-detect baseline results, 8 had detections at 4 months. At 7 of these 8 locations, 4amino-2,6-DNT SPLP results decreased at 6 months.
- Hypothesis testing and box-and-whisker plots indicate decrease in 4-amino-2,6-DNT SPLP leachate concentrations between 4-month and 6-month sampling events.





#### 2-amino-4,6-DNT

- -Not detected in any of the 6-month soil samples, as compared to baseline detection frequency of 17/19.
- Not detected in any of the 6-month SPLP leachate samples, as compared to baseline detection frequency of 8/13.
- -Strong evidence of degradation.

#### 1,3-DNB

- Hypothesis testing indicates increase in 1,3-DNB concentration between baseline and 4 months and no change between 4 months and 6 months
- On the other hand, hypothesis testing indicated baseline and 6-month soil detections are statistically the same

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-Not clear if 1,3-DNB concentrations began to decrease towards end of pilot study









#### 1,3,5-TNB

- –6-month and baseline soil results are statistically equal in 65 75 ft bgs interval and pooled 10 25 ft bgs interval
- 3,5-Dinitroaniline
- Hypothesis testing indicates no change in 3,5-dinitroaniline concentration in each interval between 4 months and 6 months
- -Box-and-whisker plots suggest 3.5-dinitroaniline concentration could be decreasing at 10-15 ft bgs

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### **PERFORMANCE MONITORING - SUMMARY**

Strong evidence for degradation of RDX, HMX, 2,4,6-TNT, 2,4-DNT, and 2-amino-4,6-DNT

Results suggest both formation and degradation of 4-amino-2,6-DNT

SPLP leachate concentrations suggest degradation of 2,6-DNT

Results for 1,3-DNB are inconclusive

Results for 1,3,5-TNB show no degradation

Degradation processes generated 3,5-dinitroaniline. Shallow soil data suggestive of a decrease in 3,5-dinitroaniline concentration between 4 months and 6 months.

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## **PERFORMANCE MONITORING – SUMMARY (CONT.)**

Location BHNE, 20 - 25 ft bgs



### **PERFORMANCE MONITORING – SUMMARY (CONT.)**

Location BHNE, 20 - 25 ft bgs



## ADDITIONAL ENERGETICS DEGRADATION PATHWAYS

#### 2,4,6-TNT

- Aerobic biodegradation can form 4-amino-2,6-DNT, which can subsequently degrade through intermediates not included in Method 8330B
- Possible that initial increase in 4-amino-2,6-DNT SPLP leachate concentrations at 8 locations reflected 2,4,6-TNT degradation (although subsurface temperatures were well above the optimal range for most bacteria – perhaps during the heating period?)

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#### 3,5-Dinitroaniline

- -Limited information available on this compound, but could be a 2,4,6-TNT degradation product.
- -Has been identified as a biodegradation product of 1,3,5-TNB.



# **COMPARISON TO 2015 PILOT STUDY**

RDX and 4-amino-2,6-DNT

-Better removal during 2019 study as compared to 2015 study

#### 1,3,5-TNB

-2015 pilot study showed 57% to >99% decrease in soil concentration at 10 of 16 sample locations.

– Alkaline hydrolysis performed better for 1,3,5-TNB than heat alone.

#### 1,3-DNB

File Name

 Explosive not detected in the 2015 pilot study baseline samples and the elevated reporting limits preclude estimation of changes in concentrations during the treatment period.

#### 2,4,6-TNT, 2,4-DNT, 2,6-DNT, HMX, 2-amino-4,6-DNT

-Both alkaline/steam enhanced hydrolysis and heat alone support degradation

#### Summary for Area V field conditions

- Heat alone as effective or more effective than alkaline hydrolysis for RDX, TNT, amino-DNTs, DNTs, and HMX

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-Alkaline hydrolysis more effective than heat alone for 1,3,5-TNB



## LESSONS LEARNED

#### Lessons learned

- -Heat-enhanced hydrolysis effectively remediated several explosives
  - RDX soil and SPLP leachate PRGs met in all but 1 sample. A longer operation period would likely achieve PRGs throughout treatment zone.
  - All 2,4,6-TNT and 2-amino-4,6-DNT results less than PRGs.
  - Note HMX, 4-amino-2,6-DNT, and 2,4-DNT are not contaminants of concern and do not have PRGs for this site.
- -Soil heating had little effect on 1,3,5-TNB and 1,3-DNB
- -Formation of 3,5-dinitroaniline needs to be studied
- Results for 70 75 ft bgs indicate explosives did not leach as a result of water addition while heating and degradation occurred outside of the active heating zone
- Extend data collection throughout the cooling period to evaluate the rate of heat loss and how much additional degradation occurred

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-Work with the analytical laboratory to expand the analytical suite to include degradation products that are not part of Method 8330B, even if it means using non-standard methods





File Name

### FUTURE TECHNOLOGY APPLICATION

**Future application** 

- -Vadose zone contamination with RDX, HMX, 2,4,6-TNT, DNT, and/or amino-DNT contamination
- –Use the subsurface's thermal inertia to optimize energy usage
- Potential to extend technology to groundwater but at a lower temperature to decrease energy requirements



### MORE TO COME FOR SIOUX ARMY DEPOT

We are generating the Feasibility Study for this site and will be looking at multiple alternatives for each of the matrices.

I am hoping to be able to incorporate innovative approaches that will reduce both the time to achieve the project goals, but also to maximize our efficiencies on cost.



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