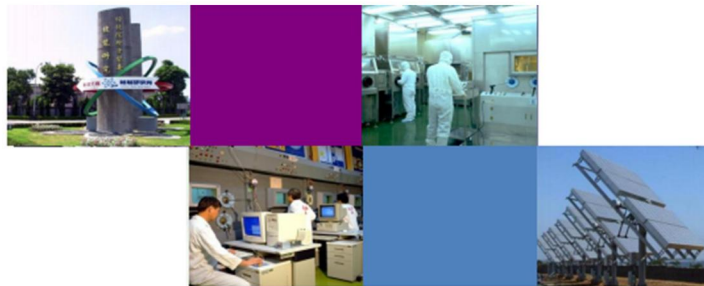# 五、附　錄

ICNST 2016 國際會議之簡報檔

ICNST 2016 : 18th International Conference on Nuclear Science and Technology
Preparation of Heterogeneous Ferrite Catalysts and Their Application for Fenton-Like Oxidation of Radioactive Organic Wastewater

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Division of Chemical Engineering, Institute of Nuclear Energy Research

Outline

- Introduction of Radioactive liquid waste stored in T61
- Solidification test of radioactive oil
- Background of heterogeneous catalysts and experimental procedure
- Fenton-like oxidation of simulated solution and radioactive aqueous wastes
- Conclusion

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Introduction (1)

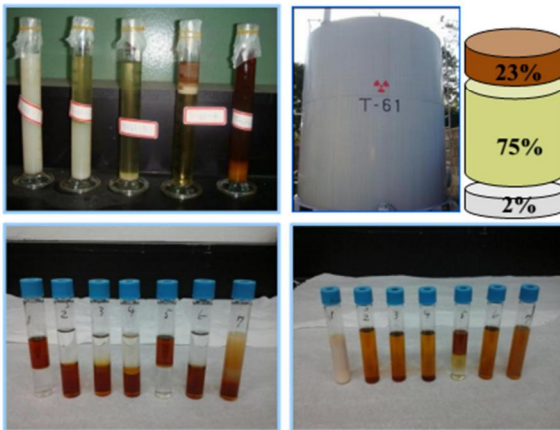➢ **Radioactive liquid wastes stored in T-61 tank**

The radioactive liquid wastes generated from nuclear application of radioisotope in **medicine industry, agriculture, hospitals, laboratory** have been transported to INER and stored in T-61 tank for tens of years.

Introduction (2)

Mixing test by miscellaneous organic solvents

➢ The liquid mixture stored in T61 tank has been separated **into three layers** by natural sedimentation
  ➢ oil phase (upper layer)
  ➢ aqueous phase (middle layer)
  ➢ bottom sludge
➢ **Oil phase**：Most organic solvents are miscible with oil, except for water and EG.
➢ **Water phase**：it contains water, miscellaneous polar solvents, and organic pollutants.

(1)water, (2) ethanol, (3) acetone, (4) acetonitrile, (5) ethylene glycol, (6) hexane, and (7) xylene.

Treatment of radioactive liquids (3)

> Treatment technologies for various radioactive oil-contained liquids

	Technology	Tritiated oils (organically bound ^3H)	Tritiated water (^3HOH) in oil	Oils with active solids	Oily water (<50% H_2O)	Oil contaminated solids
Th	Pyrolysis	Yes	Yes	Possible	Yes	No
	Plasma treatment	Yes	Yes	Yes	Yes	Yes
Ph	Absorption	Yes	Yes	Yes	Yes	Possible
	Centrifugation	No	Possible	Yes	Yes	No
	Filtration	No	No	Yes	No	Possible
	Decontamination	No	Yes	Yes	Yes	Yes
Ch	Electrochemical treatment	Yes	Yes	Possible	Yes	No
	Wet oxidation	Possible	Possible	No	Possible	No

Th = Thermal, Ph = Physical, Ch = Chemical

Please refer to : Low Level Waste Repository, LLWR
Management of Contaminated Oils, NWP-REP-086-Issue 1-Mar 2015

> In previous work, the oil phase of radioactive liquid wastes stored in T61 belongs to oils with active solids, therefore we selected absorption as the pre-treatment step, followed by incineration for volume reduction.

> Solidification was performed by using Nochar Petrobond® polymer (N910) as oil absorbents.

> The optimal ratios of oil/polymer were evaluated by experimental test, such as thermal tests (by heating) and exudation tests (by loading).

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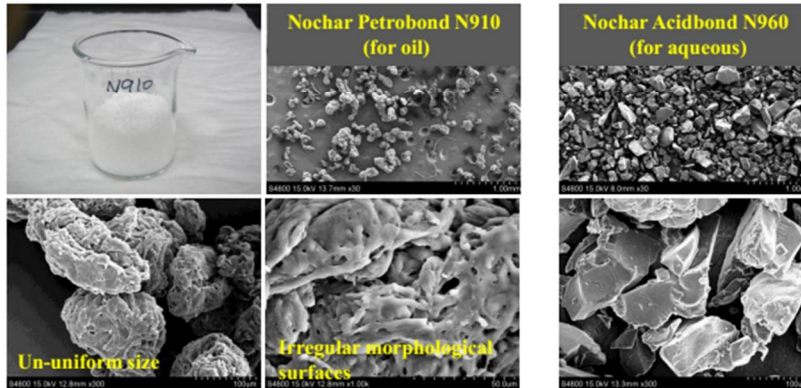> **Conclusion**

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Nochar Petrobond N910

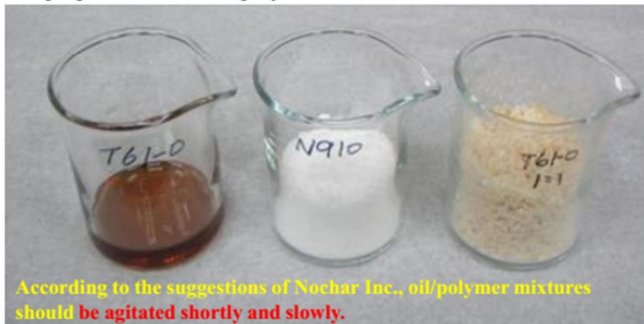➢ Nochar Inc,. provide polymer absorbent either for oil phase or aqueous phase

➢ Nochar Petrobond® N910 polymer is selected as oil absorbent for solidification of oil phase
➢ N910 polymer is white and soft powders, otherwise N960 powders show hardness
➢ After the solidification, the matrix can be stored more safely or further treated by incineration for volume reduction.

Solidification test of oil with N910 (1)

➢ Target : optimal weight ratio of oil/polymer

The proportions of oil to polymer

According to the suggestions of Nochar Inc., oil/polymer mixtures should be agitated shortly and slowly.

As oil was added into the beaker with polymer, oil was absorbed into polymer and formed brown gel-like aggregates. It is reported that there are two steps in the solidification process
1. Swelling : when oil contacted with the surface of N910, then the polymer chains were swelled
2. Curing : the swelled polymer sequentially preceded curing reaction to form chemical bonds.

Solidification test of oil with N910 (2)
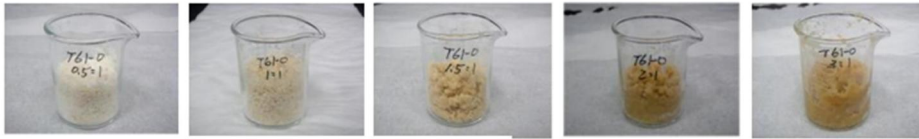
| Sample code	Weight of T61-O (g)	Weight of N910 (g)	Ratio of T61-O/N910	color	Observation
S-0510	5	10	0.5:1	Light yellow	Dry and granular aggregates
S-1010	10	10	1:1	Light brown	Dry and granular aggregates
S-1510	15	10	1.5:1	brown	Doughy and adhesive aggregates
S-2010	20	10	2:1	Dark Brown	Doughy, adhesive, and moist aggregates
S-3010	30	10	3:1	Dark brown	Doughy, adhesive, and moist aggregates

✓ r = 0.5 an r = 1
This indicated that oil has been totally absorbed by polymer molecules, thus the amount of polymer is excess to oil.

✓ r = 1.5 and 2
no granular aggregates were founded.
In the case of S-2010, the surface of the mixture even showed moist appearance and oil-absorbed polymer was found sticky on the glass surface of the beaker.

✓ r = 3
The residual oil was present on the surface of the N910 polymer, indicating matrix was probably oil-saturated.
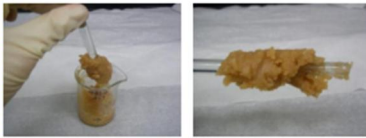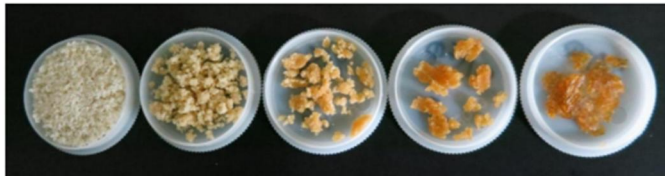
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Oil retention tests under heating(1)

➤ In order to confirm the stability of absorbed oil in polymer, the oil retention tests were conducted under **thermal condition**

➤ Sample : Around 1g of oil-polymer mixtures were first aged for 1 hr, 24 hr and 48 hr at room temperature, respectively.

➤ Oil retention tests : the aged mixtures were heated in a oven at **50˚C** for **24 hr**

➤ The remained weight percentages were calculated as following equation:

$$Residual \ oil \ (\%) = \frac{m_2}{m_1} \times 100\%$$

m_1 : weight of oil in mixture before heating

m_2 : weight of oil in mixture after heating

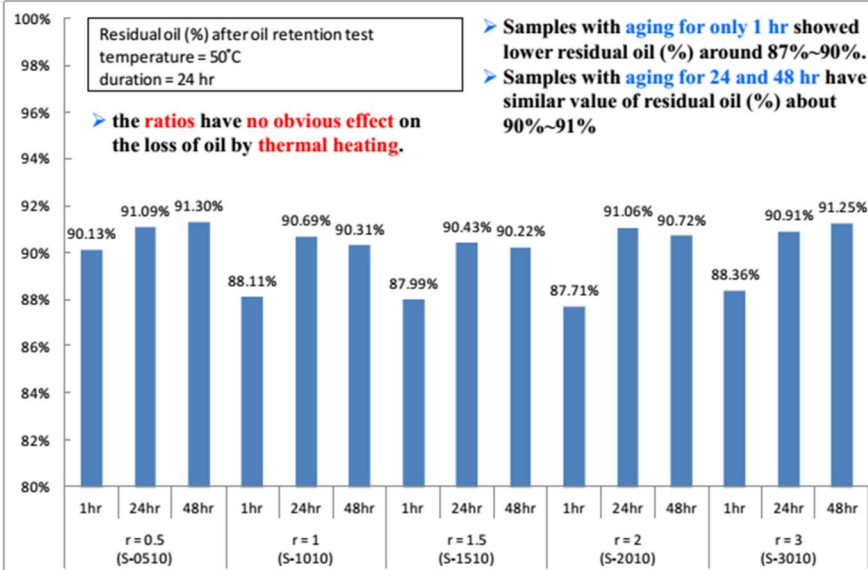Institute of Nuclear Energy Research

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Oil retention tests under heating (2)

Residual oil (%) based on total oil

Residual oil (%) after oil retention test
temperature = 50°C
duration = 24 hr

➤ the **ratios** have **no obvious effect** on the loss of oil by **thermal heating**.

➤ Samples with **aging for only 1 hr** showed lower residual oil (%) around 87%~90%.
➤ Samples with **aging for 24 and 48 hr** have similar value of residual oil (%) about 90%~91%

Chart data:
- r = 0.5 (S-0510): 1hr 90.13%, 24hr 91.09%, 48hr 91.30%
- r = 1 (S-1010): 1hr 88.11%, 24hr 90.69%, 48hr 90.31%
- r = 1.5 (S-1510): 1hr 87.99%, 24hr 90.43%, 48hr 90.22%
- r = 2 (S-2010): 1hr 87.71%, 24hr 91.06%, 48hr 90.72%
- r = 3 (S-3010): 1hr 88.36%, 24hr 90.91%, 48hr 91.25%

Exudation tests under loading (1)

➤ All samples (**after aging for 4hr, 24hr, 48 hr**) were tested by the exudation to verify the stability of oil in polymer under **external loading**.

2kg counterweight
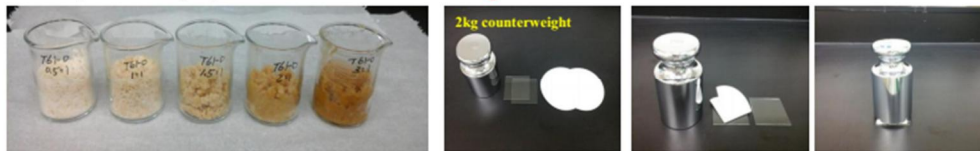
1. Around 0.2g of mixtures were first placed between two filtration papers
2. then put them between two sheet glasses under the loading for 15 minutes.

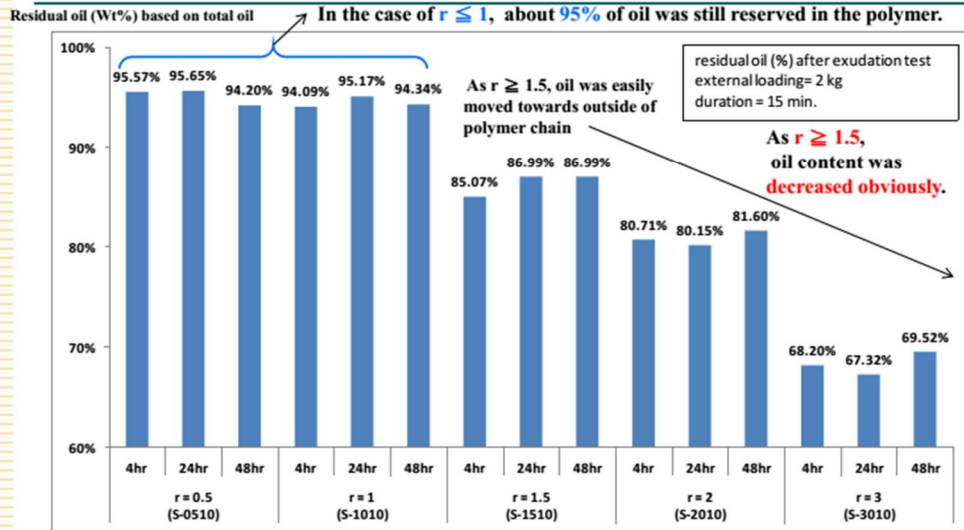r = 0.5 / 1   r = 1 / 1   r = 1.5 / 1   r = 2 / 1   r = 3 / 1
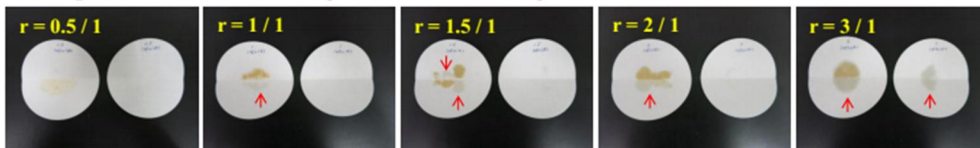
■ Except for r = 0.5 ,
  ✓ all filtration papers showed the signs of grey color
■ Grey color is the evidence of **oil exudation** from the oil/polymer mixtures.
  ✓ oil was released from polymer chains due to physical compression
■ In the case of r = 3,
  ✓ even **two** filtration paper show the sign of oil exudation, which means saturated matrix

Exudation tests under loading (2)

Residual oil (Wt%) based on total oil

In the case of r ≤ 1, about **95%** of oil was still reserved in the polymer.

As r ≥ 1.5, oil was easily moved towards outside of polymer chain

residual oil (%) after exudation test
external loading = 2 kg
duration = 15 min.

As r ≥ 1.5, oil content was **decreased obviously.**

	r = 0.5 (S-0510)			r = 1 (S-1010)			r = 1.5 (S-1510)			r = 2 (S-2010)			r = 3 (S-3010)		
	4hr	24hr	48hr	4hr	24hr	48hr	4hr	24hr	48hr	4hr	24hr	48hr	4hr	24hr	48hr
	95.57%	95.65%	94.20%	94.09%	95.17%	94.34%	85.07%	86.99%	86.99%	80.71%	80.15%	81.60%	68.20%	67.32%	69.52%

> Based on the results and economical consideration, it is believed the ratio of 1 (S-1010) is the optimal condition for the solidification of oil phase wastes

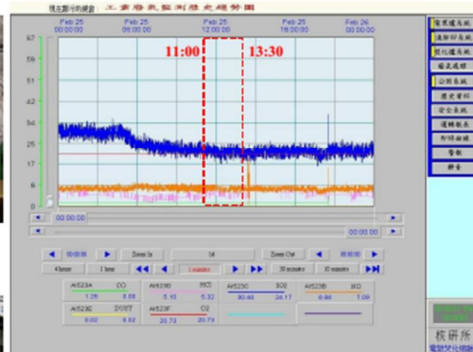Institute of Nuclear Energy Research

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Incineration of solidified matrix

Oil phase wastes

Mixing process of oil phase with Nochar N910

Solidification of oil phase forming gel-like matrix

Solidified matrix was packaged for incineration

The off gas of incineration such as SO2、NOx、HCl、 CO were about 40 ppm, which is all below the limit of regulation (180ppm、180ppm、60ppm、 100ppm).

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Treatment of waste water with high TOC

A.N. Soon, B.H. Hameed / Desalination 269 (2011) 1–16
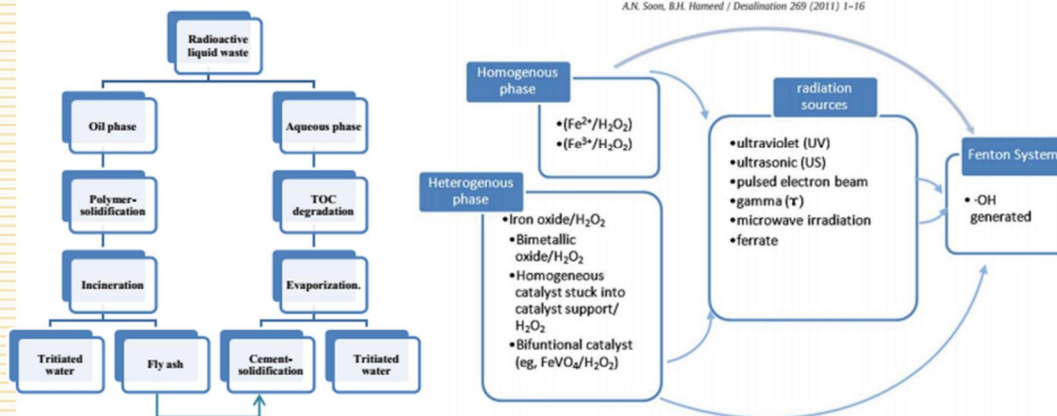
- **Fenton reagent** (H. J. H. Fenton in 1890s)： application of the treatment of wastewater containing organic pollutants.
- Heterogeneous catalyst： fewer ferric sludge, magnetic properties, inexpensive separation
- The degradation of wastewater pollutants in heterogeneous catalytic Fenton system were developed as a feasible and environmentally benign process.
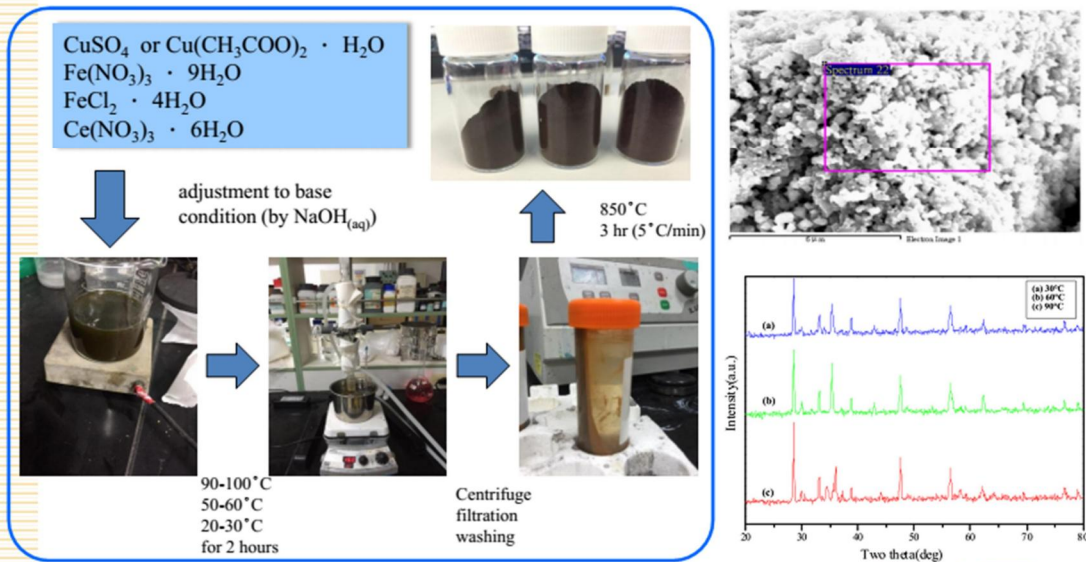
Fenton reaction for TOC degradation

	Homogeneous Fenton reaction	Heterogeneous Fenton reaction
Phase	The same phase as the reagents	Two phase of solid and liquid
Mechanism	Chemical reaction (in the degradation process)	Physical behavior(absorption and desorption) and Chemical reaction
Catalyst activity	Fast	UV, nanosized effect
Active sites	Fe^{2+}, Fe^{3+}, $Fe\text{-}OOH^{2+}$, iron complexes ion	Dispersed on surface in the form of iron oxides, iron complexes ion, iron ions
Catalyst loss	High catalyst loss after reaction takes place. Additional recovery separation steps are required for the catalyst after treatment in order to comply with the national environmental regulation	Iron loss is limited because the active phase is anchored on the surface of porous solid materials
Catalyst recovery	Possible but time consuming and cost ineffective	Ease of recovery and recycling is guaranteed
pH	Tight acidic pH range for the reaction and need pH adjustment before and after	Broad pH range
Sludge treatment	High amount of treated effluent is precipitated as ferric hydroxide sludge when the reaction solution was neutralized in the post-treatment	Minimal ferric hydroxide is formed due to leaching of the active components into the bulk solution

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Experimental steps

$CuSO_4$ or $Cu(CH_3COO)_2 \cdot H_2O$
$Fe(NO_3)_3 \cdot 9H_2O$
$FeCl_2 \cdot 4H_2O$
$Ce(NO_3)_3 \cdot 6H_2O$

adjustment to base condition (by $NaOH_{(aq)}$)

850°C
3 hr (5°C/min)

90-100°C
50-60°C
20-30°C
for 2 hours

Centrifuge
filtration
washing

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Characterization of aqueous phase in T61

Characterization of aqueous wastes

PROPERTIES OF AQUEOUS WASTE IN T61 TANK

Liquid Wastes in T61	Description
Aqueous phase	The aqueous phase is the lower layer of radioactive liquid wastes stored in T61 tank. Radioactive wastewater was composed of miscellaneous organic compounds, such as organic solvents, detergents, couple agents, and so on.
Volume (m3)	~40
Chloride content	0.7wt% of NaCl were detected
TOC (ppm)	21,600 mg/L
Radiological characterization	1.86 Bq/ml of Grossβ 1.57×10^{1} Bq/ml of Cs-137 1.81×103 Bq/ml of H-3
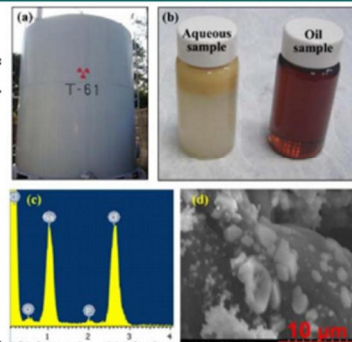
- The dried residues were analyzed by SEM/EDX to evaluate the chlorine content. According to the specific spectrum of chlorine, the obvious peaks at 2.6 KeV were found in EDS energy position analysis, thus it was verified chlorine ion was found in aqueous sample.

- Radioactive wastewater was composed of miscellaneous organic compounds, such as organic solvents, detergents, couple agents, and so on. Total organic carbon (TOC) of the wastewater is near to 22,000 ppm

Degradation of TOC of simulated solution

■ **Destruction and removal efficiency (DRE) of TOC**

$$DRE(\%) = \frac{TOC_i - TOC_f}{TOC_i} \times 100\%$$

	RUN A	RUN B	RUN C	RUN D	RUN E	RUN F
50%H_2O_2	50	60	80	80	80	80
Catalyst (g)	2	2	2	1	0	2
Time (s)	120	120	120	120	120	60
W_{TOCi} (mg)[a]		2968				
W_{TOCf} (mg)[b]	641	173	1	6	1502	576
C_{TOC} (mg/L)	5770	1370	7	44	8630	3535
DRE (%)	78.40	94.17	99.97	99.80	49.39	80.59

Run	C_{TOC} (mg/L)	W_{TOC} (mg)	DRE (%)
1st	8.29	1.33	99.96
2nd	8.70	1.40	99.95
3rd	8.25	1.33	99.96
4th	7.34	1.24	99.96
5th	7.96	1.27	99.96
6th	8.62	1.39	99.95
7th	8.40	1.37	99.95
8th	7.30	1.18	99.96
9th	8.31	1.34	99.95
10th	7.97	1.38	99.95

Volume of MeOH solution: 100 m (TOC = 29682 mg/L)
Adding rate of 50%H_2O_2 : 2.5ml/min
Reaction temperature: 95 ˚C
[a] W_{TOCi}: initial weight of TOC before Fenton-like oxidation reaction
[b] W_{TOCf}: final weight of TOC after Fenton-like oxidation reaction

The effects on degradation of TOC
■ amount of **H_2O_2** ：the source of · OH
■ amount of **catalyst** ：active site for oxidation
■ reaction **time** ：conversion

Organic wastewater: 10% MeOH, 100 mL,
initial TOC = 29,682 mg/L;
Oxidant: 50% H2O2, 80 mL, 2.5 mL/min;
Catalyst: magnetic catalyst, 2g;
Reaction temperature: 95~100 C;
Reaction time: 120 min.
Repeat runs of degradation of TOC
■ For 10 runs, DREs are not decreased.
■ **Blue solution** formed

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Degradation of TOC of simulated solution

	RUN 1	RUN 2	RUN 3
Simulated wastewater	10% IPA	10% MeOH	20% MeOH
W_{TOCi} (mg)[a]	4712	2968	5936
W_{TOCf} (mg)[b]	789	1	2729
C_{TOC} (mg/L)	4933	7	16438
DRE (%)	83.25	99.97	54.03
pH	3.25	6.93	2.09

	RUN 4	RUN 5	RUN 6	RUN 7	RUN 8
	Homogeneous catalyst		Heterogeneous catalyst		
Catalyst	$FeSO_4$ ·7H_2O	$Fe(C_2O_4)$·2 H_2O	Fe-200	$CuFe_2O_4$	CFCO
W_{TOCi} (mg)[a]			2968		
W_{TOCf} (mg)[b]	13	20	1337	624	791
C_{TOC} (mg/L)	115	175	10780	5625	6590
DRE (%)	99.56	99.33	54.96	78.98	73.35
pH	1.91	5.25	2.02	2.29	2.40

Volume of simulated solution: 100 ml
50%H_2O_2: 80 ml at adding rate of 2.5ml/min
Amount of CFCO catalysts: 2g
Reaction condition: 95 ˚C for 120 min
[a] W_{TOCi}: initial weight of TOC before Fenton-like oxidation reaction
[b] W_{TOCf}: final weight of TOC after Fenton-like oxidation reaction

The effects on degradation of TOC
■ **kinds of pollutants** ：the rate of destruction mechanism
■ **concentration of pollutants** ：it needed to increase the amount of H_2O_2 to perform the oxidation reaction to degrade the redundant MeOH molecules in solution.

Volume of MeOH solution (10%): 100 ml (TOC = 29682 mg/L)
50%H_2O_2: 50 ml at adding rate of 2.5ml/min
Amount of CFCO catalysts: 2g
Reaction condition: 95 ˚C for 60 min
[a] W_{TOCi}: initial weight of TOC before Fenton-like oxidation reaction
[b] W_{TOCf}: final weight of TOC after Fenton-like oxidation reaction

The effects on degradation of TOC
■ **homogeneous oxidation** ：high efficiency and sludge formed
■ **Cu or Ce contained catalysts** ：better than Fe-200 powders, which means Cu/Ce metal could improve the efficiency of Fenton oxidation reaction

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Degradation of TOC of aqueous waste of T61

	RUN 9	RUN 10	RUN 11	RUN 12	RUN 13
C_{TOCi} (mg/L)[a]			21600		
CFCO catalyst (g)	0	0	2	2	2
H_2O_2 (ml)	0	80	20	40	80
C_{TOCf} (mg/L)[b]	9162	491	151	109	3

Volume of aqueous waste from T61: 100 ml
50%H_2O_2: adding rate of 2.5ml/min by drops
Reaction condition: 95°C for 120 min
[a] C_{TOCi}: initial concentration of TOC before Fenton-like oxidation reaction
[b] C_{TOCf}: final concentration of TOC after Fenton-like oxidation reaction

pump

glass reactor

condenser

oil bath

■Run9：the vaporized organic component with low boil point could not trapped by the condenser, leading to the reduction of TOC concentration in aqueous waste samples (distillatory)

■Run 10：role of H_2O_2 ： TOC concentration was reduced from 9162 to 491 ppm. The aqueous wastes were degraded in the presence of H_2O_2 even without catalysts.

■Run 11~13：the amounts of H_2O_2 was benefit for the TOC degradation from 151 to 3 ppm by using 20 to 80 ml of H_2O_2.

■RUN 9 ~ RUN 13：the performance of Fenton-like oxidation of aqueous waste was depend on the presence of CFCO catalysts and the amount of H_2O_2 added.
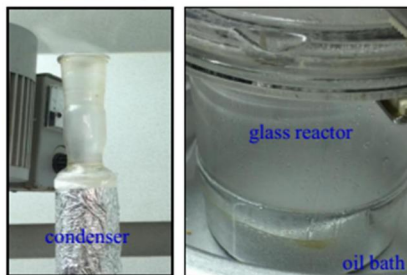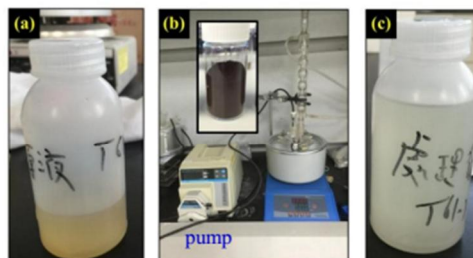
Conclusion

■ In this work, ferrite-based catalysts (CFCO) were prepared and applied in the Fenton-like oxidation reaction by comparison with homogeneous water-soluble catalysts and commercial available catalysts.

■ According to the results of catalytic oxidation, the TOC concentration of either simulated solution or aqueous radioactive wastes were reduced obviously without forming sludge or wet secondary wastes.

■ The results of TOC decomposition efficiency around 54% ~ 99% were obtained when the catalyst loading, H_2O_2 loading, and reaction time were controlled.

Thanks for your attention !!
Q & A