In-Situ Generated Ferrate as a Treatment Reagent for PFAS-contaminated Landfill Leachate Wastewater

KEITH MCLEROY
Ecolyse
College Station, Texas

VLADIMIR DOZORTSEV, Ph.D.
AMS
Sunnyvale, California

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ABSTRACT

A novel in-situ electrolytic ferrate (Fe^{+6}) generation system has been developed, enabling the on-demand production of high concentrations (> 7,000 ppm) of a fresh Fe^{+6} treatment reagent on-site. This breakthrough technology (AMS's SafeGuard™ H2O) offers a sustainable solution for addressing per- and polyfluoroalkyl substances (PFAS) contamination in landfill leachate; it has demonstrated effective removal of various PFAS compounds, and it has oxidized organic residuals in leachate. Results will be presented.

INTRODUCTION

With landfill operators facing increasingly stringent water quality regulations, managing PFAS in leachate has become a critical issue for landfills striving to meet environmental standards and protect public health. Separation technologies, primarily membrane filtration, have emerged as an effective solution for PFAS concentration and purification. However, while these systems have been effective for PFAS removal, the rejected wastewater (concentrate) contains a significantly higher concentration of PFAS than the original leachate, making it crucial to manage this hazardous and toxic waste stream properly.

The effectiveness of ferrate (Fe^{+6}) species in degrading different PFAS compounds has been broadly studied and is well documented. A Fe^{+6} reagent has demonstrated the ability to effectively oxidize and breakdown carbon-fluorine bonds across different sample matrices and under a wide range experimental conditions (Bates et al, 2014; McBeth and Graham, 2021). While Fe^{+6} has the capacity to address PFAS compounds in wastewater and other water-based matrices due to its outstanding oxidizing power, synthesis difficulties and the inherent instability of bulk Fe^{+6} has made its application restrictive.

Now, with the development of a proprietary Fe^{+6} generation system, ferrate can be generated in-situ, on-demand electrolytically, providing a high-yield Fe^{+6} reagent sufficient for industrial implementation. The fully automated generation system produces a fresh Fe^{+6} reagent concentrate at site, with a high concentration (> 7,000 parts per million (ppm)), that is scalable and capable of treating a broad range of PFAS-impacted waters to achieve treatment goals.

The ferrate generation system's electrolytic process requires only three consumables: a sacrificial iron anode, a caustic solution and electricity. The electrolytic approach is a one-step process in which the electrolyte is continuously fed into the electrolytic unit while the outflowing Fe^{+6} reagent is dosed into the treated flow. The ferrate generation system has an inline ferrate concentration monitor to ensure a stable Fe^{+6} generation process.

A study was undertaken at a water research facility in College Station, Texas to evaluate the electrogenerated Fe^{+6} as a PFAS treatment reagent in PFAS-contaminated landfill leachate wastewater. The study also investigated the effect of Fe^{+6} reagent doses on PFAS treatment efficiency. Supplementary, the effect of organic residual level in the leachate samples (Total Organic Carbon (TOC)), on PFAS removal efficacy was studied to optimize the PFAS treatment process.

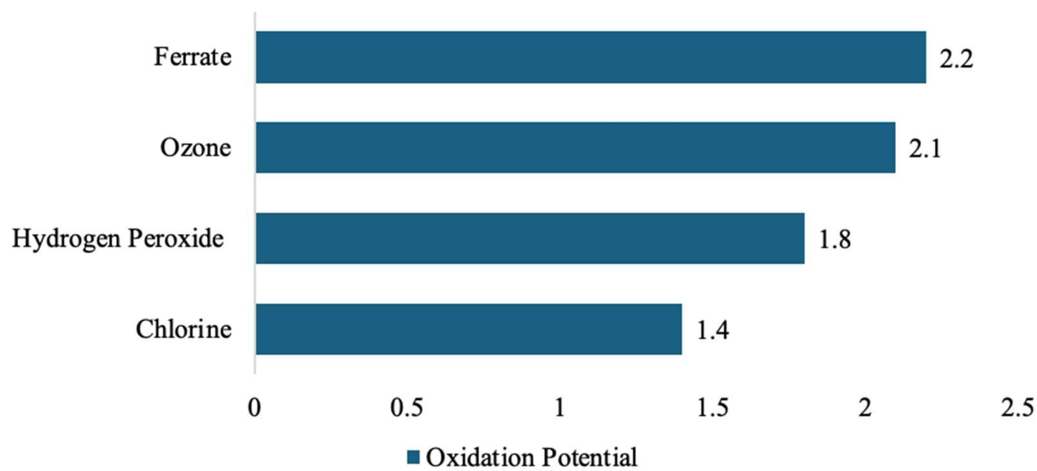
Samples of PFAS-contaminated landfill leachate wastewater were sent to the testing facility. Initial testing was done using on-demand freshly generated Fe^{+6}; frozen samples of on-site-generated Fe^{+6} reagent will also be used.

The evaluation showed that the advanced electrogeneration system could generate a Fe^{+6} reagent solution on-site and on-demand capable of effectively treating an extensive range of PFAS group compounds and remediate them from the water matrix. Most notable was that the high concentrated levels of Fe^{+6} generated on-site provided an overwhelming oxidative degradation of PFAS and the organic residuals not recently seen in previous research publications. This evaluation also afforded a progressive discovery to address the inherent problems of Fe^{+6} synthesis difficulties, instability, yield and concentration.

THE EFFICACY OF FERRATE

Ferrate (FeO4)2-, first synthesized in Germany in 1715, is a supercharged form of iron with a +6 oxidation state, also known as Fe^{+6}. It is one of the strongest oxidants known (Figure 1). Its oxidation potential is higher than ozone's and almost twice that of chlorine (Metcalf & Eddy, 2003), and it is capable of solving a range of treatment challenges, unlike other common oxidants. Fe^{+6} has been demonstrated to effectively oxidize, coagulate, and remove a wide range of contaminants of concern (Table 1).

Figure 1: The Standard Oxidation Potential for Chemical Disinfectants



Adapted from Metcalf & Eddy (2003), Wastewater Engineering Treatment and Reuse, Fourth Edition, McGraw Hill.

Table 1: Summary of Published Fe^{+6} Removal Efficiency Rates by Contaminant and Pollution Scenario

Contaminant	*Pollution Scenario*	*% Removal*
Triclosan	Pharmaceuticals	65.5%
Amoxicillin	Pharmaceuticals	76.3%
Naproxen & Ciprofloxacin	Pharmaceuticals	50 - 70%
Trimethoprim	Pharmaceuticals	91%
sulfamethoxazole	Pharmaceuticals	36%
Methylene Blue & Remazol Black Blue	Dyes Removal	~ 100%

Azo Dye Orange II	Dyes Removal	95.6%
Azo Dye Reactive Brilliant Red X-3B	Dyes Removal	99%
2-benzylphenol, phenol, chlorophene and 4-chlorophenol	Endocrine Disruptors	~ 100%
4-tert-octylphenol (TOP) & 17α-ethynylestradiol (EE2)	Endocrine Disruptors	80 – 100%
perfluorooctansulfonate	PFAS	34%
perfluorooctanoic acid	PFAS	23%
Turbidity	Produced Water	95.07% - 97.66%
COD	Produced Water	74%
Microbial by-product-like matter	Produced Water	64%
Acid-like components	Produced Water	43%

Fe^{+6} is environment-friendly, and when applied to organic-containing waters, it does not create toxic disinfection by-products (DBPs). It rapidly decomposes to ferric iron, precipitating quickly from the solution. Because the residual is non-toxic ferric iron, it can be safely land-applied for disposal or recycled. However, synthesis difficulties and the inherent instability of bulk Fe^{+6} has made its application restrictive.

GENERATING FERRATE ONSITE

Two generation approaches are suitable for onsite ferrate reagent production:

- Wet oxidation method
- Electrolytic method

WET METHOD - In the wet oxidation approach, ferric salt (typically acidic ferric chloride) is oxidized into Fe^{+6} by strong oxidizers in concentrated caustic solution. Typically, sodium hypochlorite is used as an oxidizer in this process. The reaction equation is shown in Equation (1):

$$2FeCl_3 + 3NaClO + 10NaOH \rightarrow 2Na2FeO_4 + 9NaCl + 5H_2O \quad (1)$$

The wet method's disadvantages and limitations result from the reaction stoichiometry and the nature of the ingredients used. As it follows from the reaction, it is material-intensive and involves multiple reagents, including highly acidic ferric chloride solution, concentrated bleach solution, as well as relatively high amounts of concentrated caustic solution. Ferric chloride is an acidic and highly corrosive chemical. Bleach solution is unstable and tends to decompose releasing hazardous chlorine gas. Both reagents pose environmental and health risks during their transportation, storage and handling. Ferrate produced using this approach is not pure and contains a significant amount of sodium chloride, bleach and chlorine residuals along with potential ferric chloride co-contaminants such as trace metals.

Also, chlorine residuals in the ferrate product may cause excessive levels of DBPs in the treated water. For the generation of one mole of sodium ferrate, five moles of caustic are required. In fact, caustic consumption is even higher because some caustic is consumed by the excessive acidity of the ferric chloride reagent. Finally, the wet ferrate generation process is a batch method that requires bulky equipment and has a relatively low ferrate yield, resulting in high reagent costs.

ELECTROLYTIC METHOD - The electrolytic approach to on-demand sodium ferrate reagent generation is straightforward and relatively simple. The approach is based on membrane electrolysis of an iron anode in sodium hydroxide electrolyte according to electrode reactions (Equations 2-4).

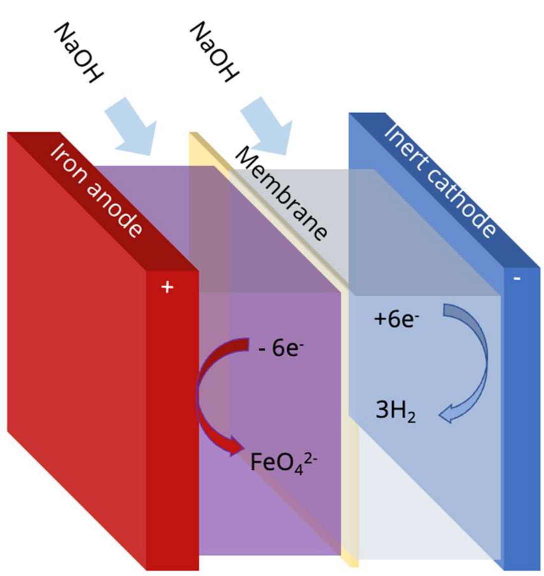
$$\text{Reaction at Anode: } Fe + 8OH^- \rightarrow FeO4^{2-} + 4H_2O + 6e^- \quad (2)$$

$$\text{Reaction at Cathode: } 3H_2O + 6^{e-} \rightarrow 3H_2 (\uparrow) + 6OH^- \quad (3)$$

$$\text{Overall Reaction: } Fe + 2OH^- \rightarrow FeO_4^{2-} + 3H_2 + 3H_2O \quad (4)$$

In this method (Figure 2), the iron anode precursor corrodes under controlled conditions, producing high valence sodium ferrate (Fe^{+6}) selectively into the electrolyte (Equation (2)). As a result of the cathode reaction, water molecules split into hydrogen gas and hydroxyl ions (Equation (3)). As it is seen from reactions (Equations (2-4)) this electrolytic process requires only three consumables: sacrificial iron anode, approximately 20-40% caustic solution and electricity. It should be noted that the relatively low caustic demand in the electrolytic method is the result of the significant amount of caustic produced during the electrolytic process on the cathode (Equation (3)), which makes this approach more economical.

Figure 2: Electrolytic Method to Generate Fe+6 Onsite

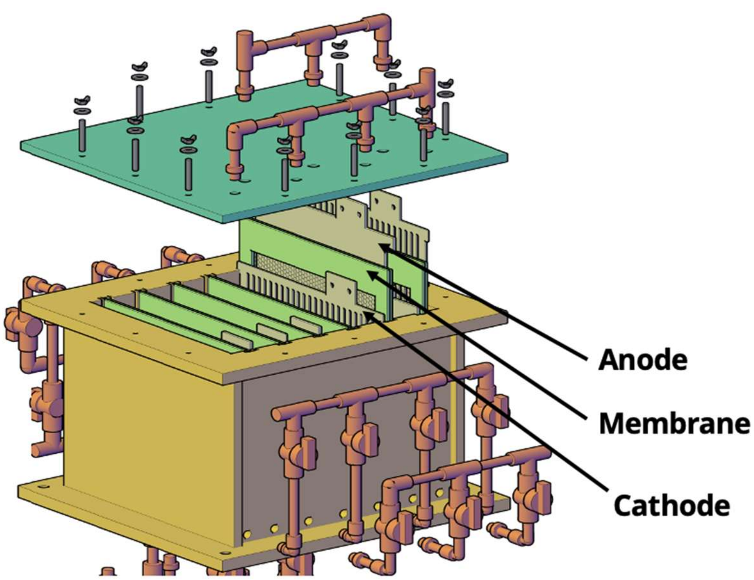


Factors such as anode composition, current density and strength of electrolyte govern the production of Fe^{+6}.

ONSITE ELECTROLYTIC FERRATE GENERATION SYSTEM

The development of a proprietary Fe^{+6} generation system enables ferrate to be generated in-situ, on-demand electrolytically (Figure 3). The major advantage of electrochemical synthesis is its simplicity and no costly chemical requirement. The approach provides a high-yield Fe^{+6} reagent sufficient for industrial implementation. The high effectiveness of the Fe^{+6} generation approach is due to the optimal design of both the flow-through electrolytic device and its operating conditions. The proprietary anode de-passivation mechanism implemented in the electrolytic process allows for long-term anode stability and reliable ferrate generation in a fully automated, continuous manner.

Figure 3: Proprietary Fe^{+6} Generation System



The Fe^{+6} generation modules are equipped with an inline ferrate concentration monitor which ensures a stable ferrate generation process and overall process integrity.

The compact, modular, and flexible design of the electrolytic unit allows the construction of ferrate generating capacity to treat virtually unlimited volumes of contaminated water:

- System Productivity: 10 kg/day (as Na_2FeO_4)
- Reagent Concentration: 20.0 g/l
- Reagent Volume: 100 gal/day
- Power Consumption: 6kWh/kg Na_2FeO_4

The electrolytic approach is a one-step process in which the electrolyte is continuously fed into the electrolytic unit, while the outflowing ferrate reagent is dosed into the treated flow or frozen for future use.

STUDY

BACKGROUND - As landfill operators face increasingly stringent water quality regulations, the challenge of controlling PFAS in leachate becomes increasingly important for maintaining compliance and protecting public health.

Separation technologies such as membrane filtration are widely used to concentrate and remove PFAS from landfill leachate. Despite their effectiveness in PFAS removal, these methods generate a concentrate stream with PFAS levels far exceeding those found in untreated leachate. Consequently, careful management and proper disposal of this concentrated waste are essential to minimize environmental risks, as highlighted throughout this paper.

The safe removal and destruction of PFAS-contaminated landfill leachate wastewater has traditionally come with a significant cost because the available treatment solutions can be energy-intensive and expensive. A cost-effective and sustainable method of PFAS removal from landfill leachate wastewater is needed.

A study was undertaken at a water research facility in College Station, Texas to evaluate the electrogenerated Fe^{+6} as a PFAS treatment reagent in PFAS-contaminated landfill leachate wastewater.

The study investigated the effect of Fe^{+6} reagent doses on PFAS treatment efficiency. Additionally, the effect of organic residual level in the leachate samples (TOC) on PFAS removal efficacy was studied to optimize the PFAS treatment process.

METHODS - Samples of PFAS-contaminated landfill leachate wastewater, containing levels near 43.0 ppm, were sent to the testing facility. Approved sampling guidelines, including sample volume preservation methods and chain-of-custody procedures, were followed.

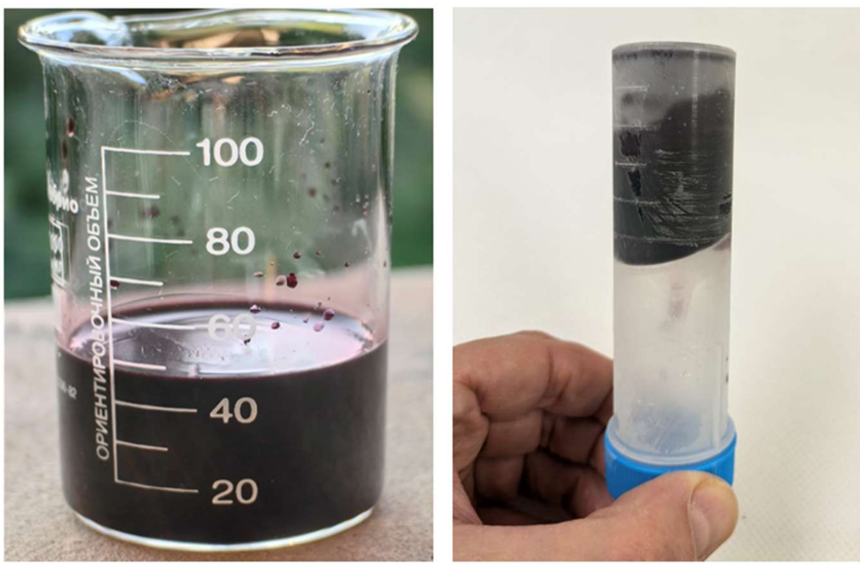
- Samples were collected per EPA Method 533
- PFAS analyses were per EPA Method 533
- PFAS calibration standards were obtained from Waters ERA

Calibration curves were established per EPA Method 533, with sample curves added to enhance PFAS detection limits to lower levels and to determine additional PFAS compounds that are not present in the ERA standards. Quality Assurance and Control methods were carried out per Method 533 requirements, in addition to precision and accuracy calculations for confirming results and instrumentation performance.

RESULTS - On-site-generated Fe^{+6} reagent was used to treat the leachate sample; frozen Fe^{+6} reagent samples will be used in future tests (Figure 4).

- The sample of PFAS-contaminated landfill leachate wastewater was pH adjusted to 5.0
- Two Fe^{+6} doses of 50 ppm each were applied with a 30-minute stirring period between doses (100 ppm total Fe^{+6} dose)
- The sample was filtered through glass fiber to remove iron oxide particulates
- Pre-treatment of the leachate sample, prior to application of the ferrate, was ozonation under the following conditions: 2000 ppm of ozone for one hour
    - TOC level in untreated leachate: 69.7 ppm
    - TOC level in leachate after ozonation: 33.83 ppm, a 52.12% reduction

Figure 4: Onsite Generate Fe^{+6} Solution, 12 g/l Na_2FeO_4 solution on left and frozen form on right



The electrogenerated Fe^{+6} reagent solution effectively degraded an extensive range of PFAS group compounds by 97.5% (Table 2) and oxidized TOC by an average of >85.0%.

Table 2: PFAS Removal Results for Onsite Generated Fe^{+6} Reagent

Specie	*RT (min)*	*Concentration (ppm)*		*% Removal*
		Initial	*Final*	
6:2 FTS	14.22	1.38	ND	100
8:2 FTS	18.24	0.18	ND	100
PFBA	3.11	1.92	ND	100
PFOA	14.37	6.39	ND	100
PFBS	8.85	42.17	0.84	98
PFPeS	10.39	0.19	ND	100
PFHxS	12.42	1.71	0.53	69
Total		53.94	1.37	97.5

CONCLUSION

It is known that ferrate Fe^{+6} has the capacity to degrade a broad range of PFAS compounds in wastewater and other water-based matrices due to its outstanding oxidizing power. Historically, because of synthesis difficulties and the inherent instability of Fe^{+6}, yielding sufficient volume quantities has been challenging, and generating a high reagent dose concentration has been restrictive.

With the development of a proprietary Fe^{+6} generation system, ferrate can now be generated in-situ, on-demand electrolytically, providing a high-yield Fe^{+6} reagent sufficient for industrial implementation. There is no other technology available that generates Fe^{+6} in-situ.

The fully automated generation system produces a fresh Fe^{+6} reagent concentrate onsite, with a high concentration that is scalable and capable of treating a broad range of PFAS-impacted waters to achieve treatment goals.

An evaluation of the technology showed that the advanced electrogeneration system could generate a Fe^{+6} reagent solution capable of effectively degrading an extensive range of PFAS group compounds by 96.0% and oxidizing the TOC by an average of >85.0%. This technology offers a sustainable solution for addressing PFAS contamination in landfill leachate.

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