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Optimizing the Treatment of Produced Water and Flowback for Reuse or Disposal

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Produced Water and Flowback: Characteristics of Concern for Reuse and Disposal

- Dissolved solids
  - soluble species like sodium, calcium, barium, chloride, sulfate
  - processes or operations like reverse osmosis, ion exchange, and chemical precipitation are required to remove dissolved solids
- Suspended solids
  - particles like sand, metal sulfides, clay, bacteria
  - suspended solids may be either settleable (e.g., sand) or colloidal (e.g., clay, bacteria)
- Scale formation potential
  - Examples: calcium carbonate (calcite), barium sulfate (barite)
- Iron and manganese
- pH

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Treatment of Produced Water and Flowback by Coagulation-Flocculation-Sedimentation

- ***Settleable solids*** are large enough to be removed from water by settling under the influence of gravity (e.g., sand)
- ***Colloidal particles*** are too small to be removed from water by settling under the influence of gravity
  - ➢ colloidal particles can be converted into settleable particles by *coagulation* and *flocculation*
- ***Coagulation*** is the process of destabilizing colloidal particles so they can grow into larger, settleable particles
  - ➢ coagulation changes the surface chemistry of colloidal particles in a way that causes them to stick together when two particles collide
- ***Flocculation*** causes colloidal particles to grow into larger, settleable particles
  - ➢ flocculation induces collisions between particles

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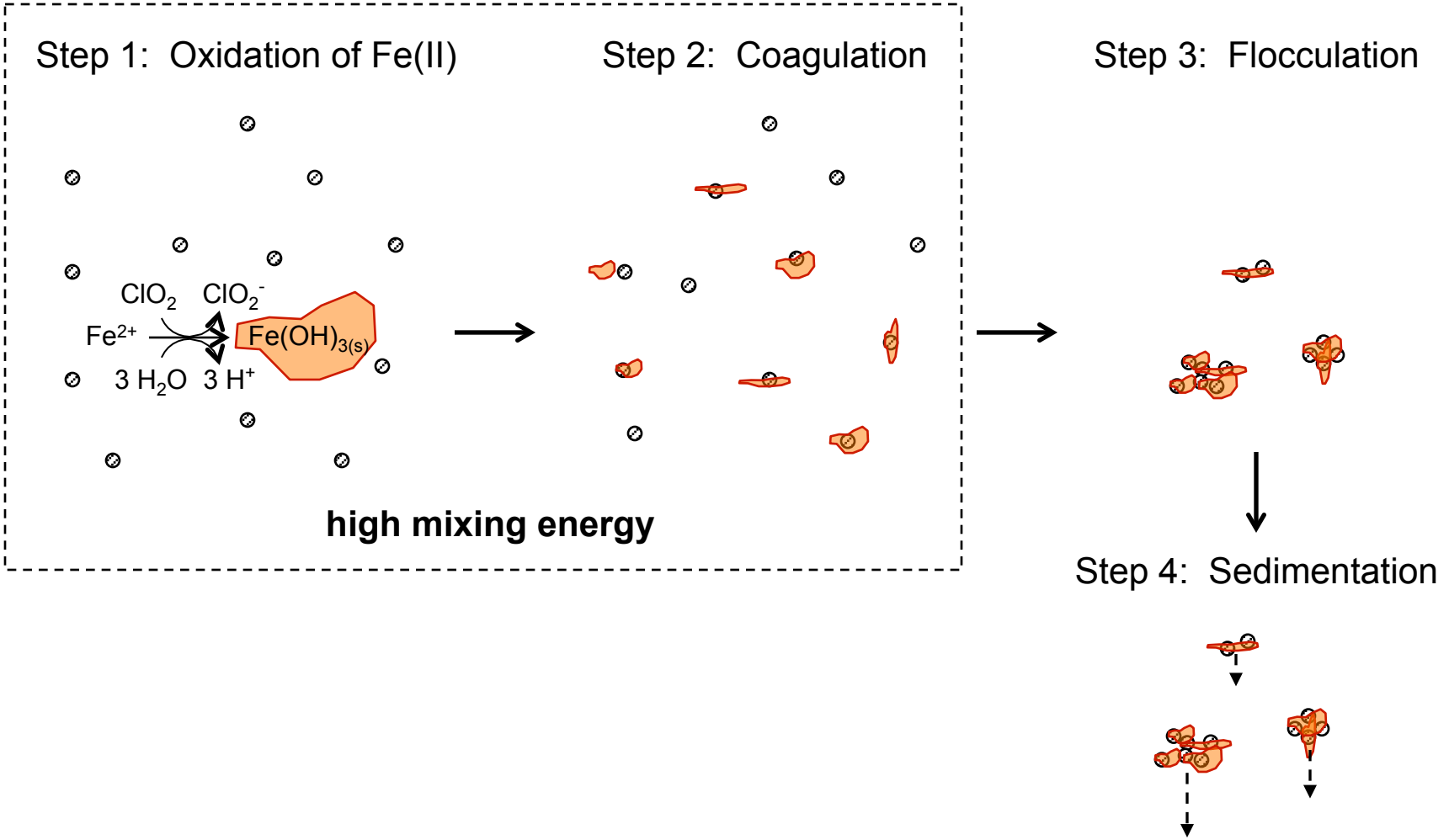
Removal of Colloidal Suspended Solids from Produced Water



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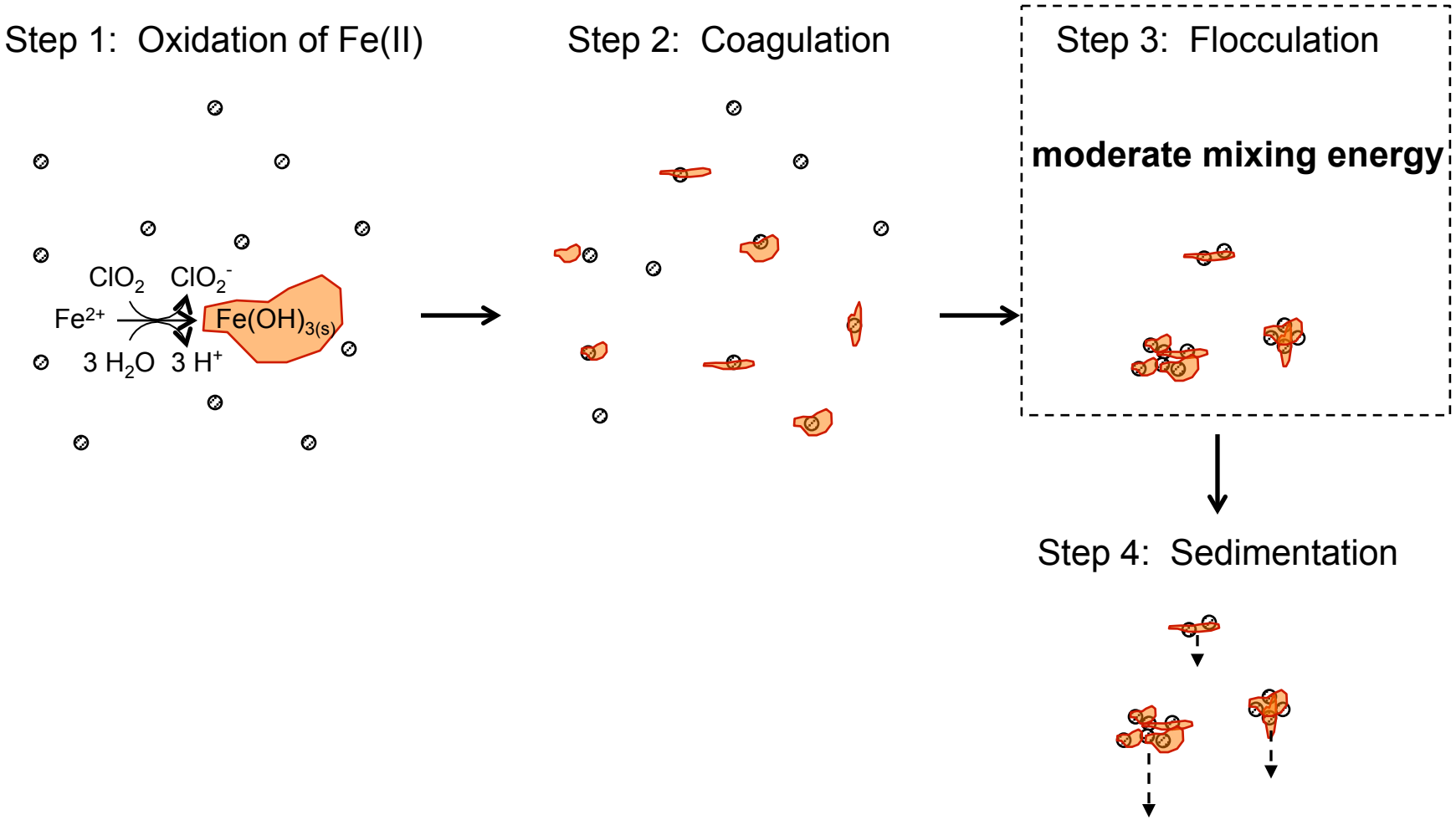
Removal of Colloidal Suspended Solids from Produced Water



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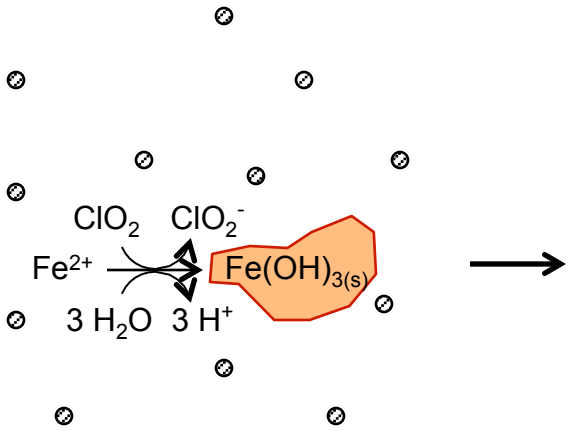
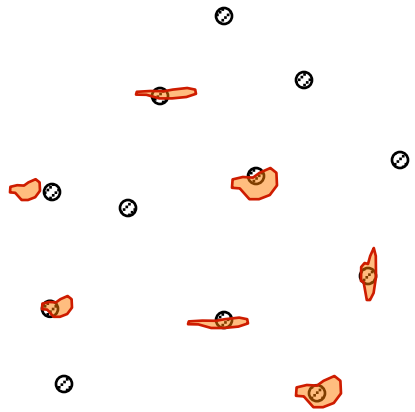
Removal of Colloidal Suspended Solids from Produced Water

Step 1: Oxidation of Fe(II)

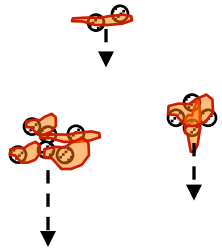


Step 2: Coagulation



Step 3: Flocculation

Step 4: Sedimentation



low mixing energy

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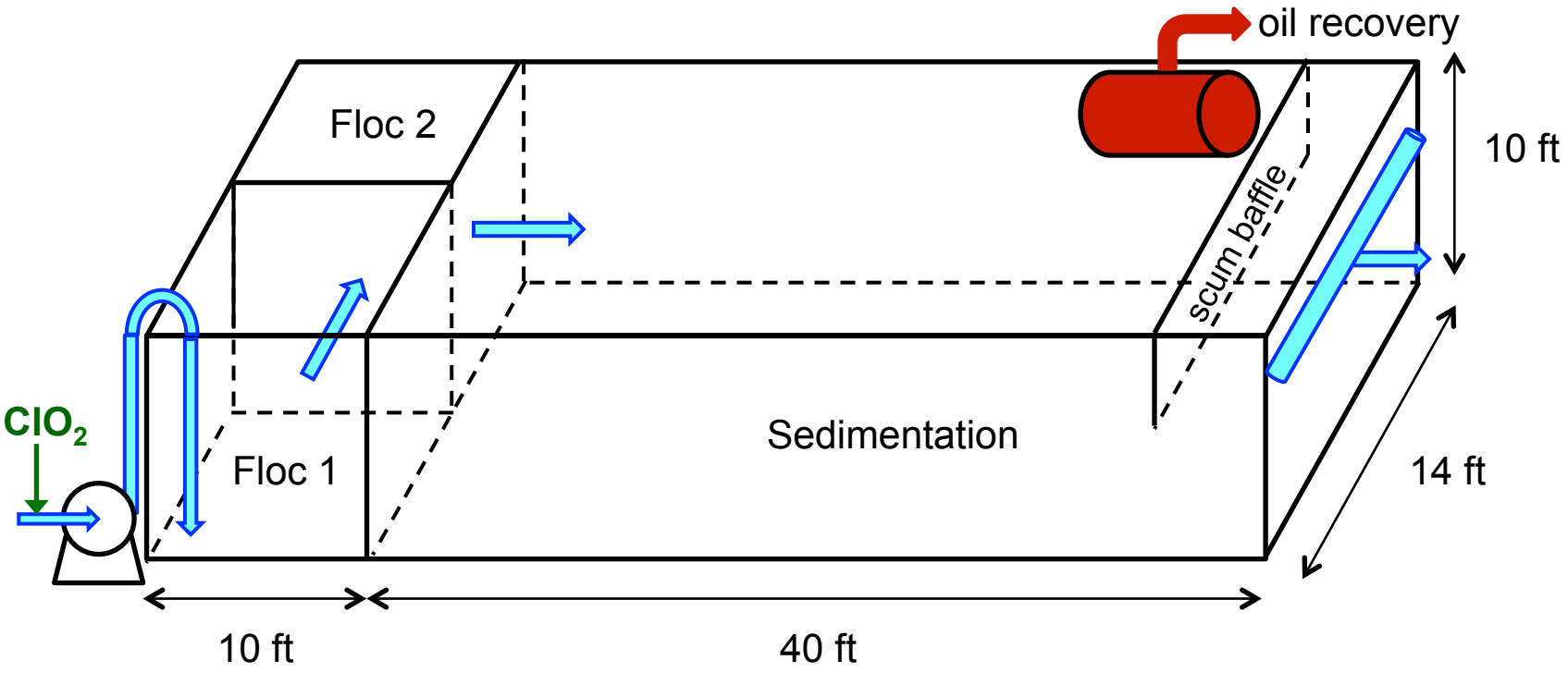
Oil-Field Implementation of Coagulation-Flocculation-Sedimentation



Has been used successfully at 7,500 bbl/day

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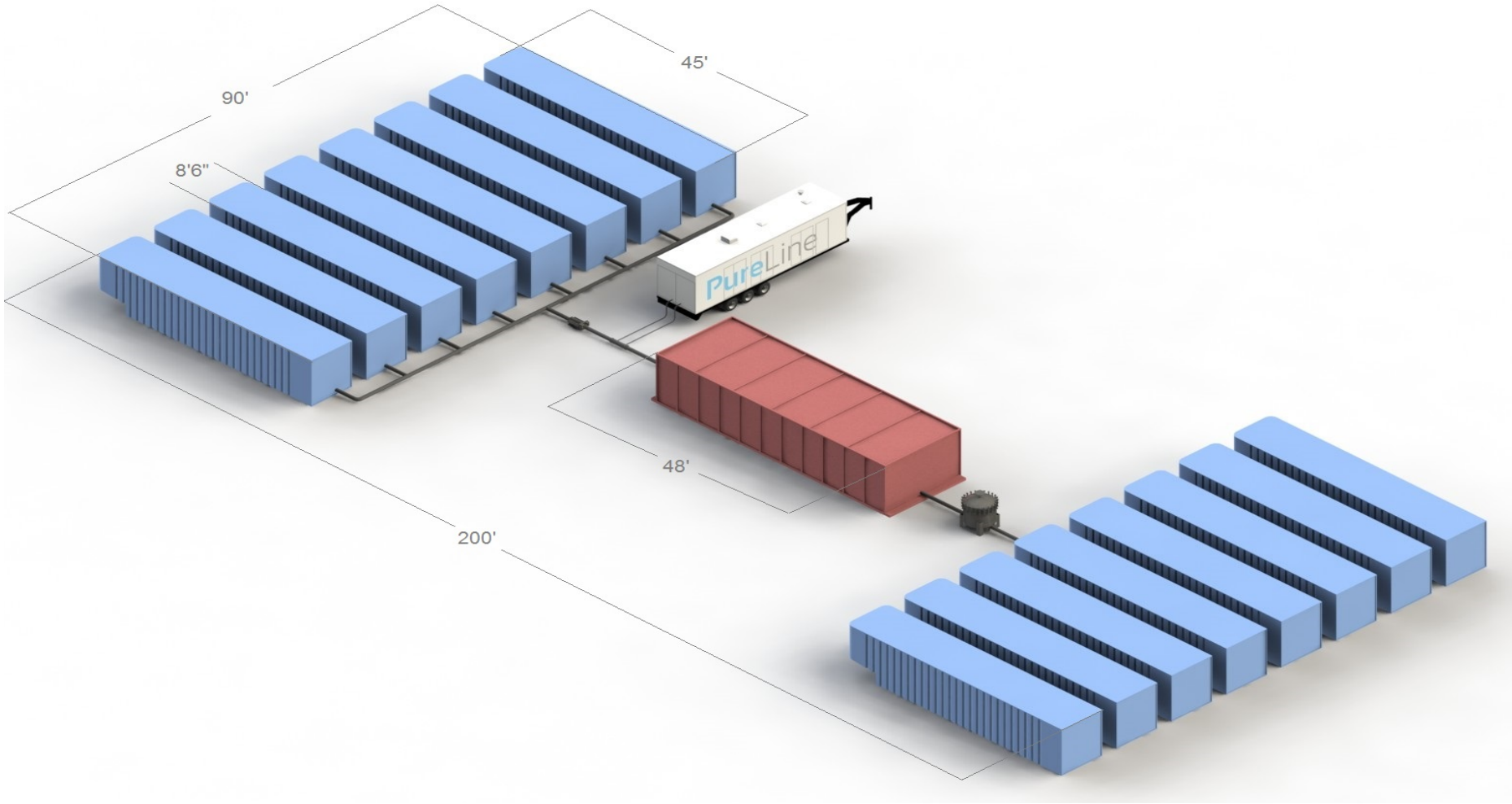
Typical Footprint



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Coagulation-Flocculation-Sedimentation Bench Test: Texas

	control	35 ppm	80 ppm	150 ppm	230 ppm
before treatment					
beginning of flocculation					
settle for 2 hours					

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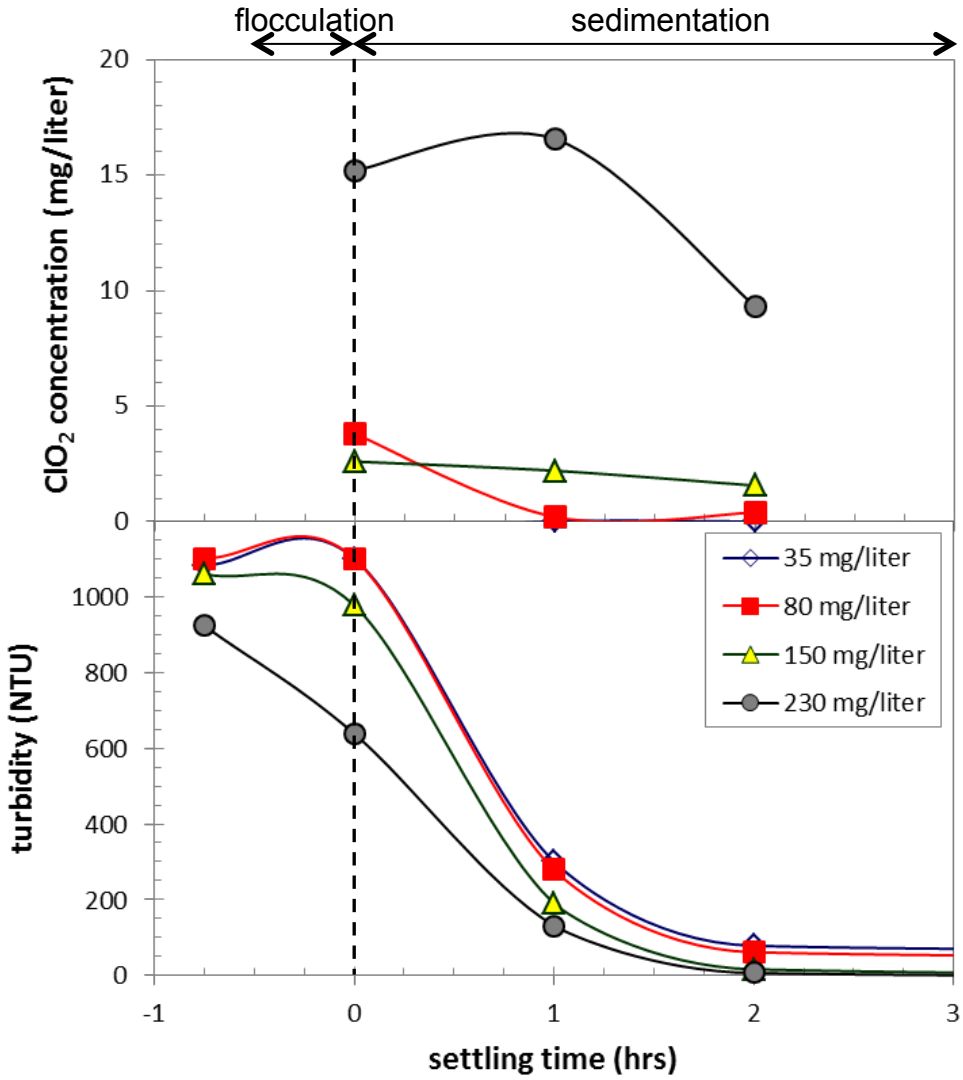
Coagulation-Flocculation-Sedimentation Bench Test Results: Texas



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Coagulation-Flocculation-Sedimentation Bench Test Results: Texas

parameter	units	treatment	
		untreated	230 mg ClO_2/liter
sodium	mg/liter	35,200	33,200
potassium	mg/liter	422	370
calcium	mg/liter	4,580	3,940
magnesium	mg/liter	595	520
barium	mg/liter	**15.4**	**2.6**
strontium	mg/liter	**1,050**	**870**
iron	mg/liter	**167**	**1.0**
manganese	mg/liter	**1.1**	**0.1**
chloride	mg/liter	65,260	55,000
alkalinity	mg/liter as $CaCO_3$	**335**	**118**
sulfate	mg/liter	164	188
total sulfides	mg/liter	**25**	**BDL**
total suspended solids	mg/liter	**3,960**	**80**
turbidity	NTU	**>1100**	**6**
pH		6.9	6.5
density	mg/liter	1.07	1.07

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Coagulation-Flocculation-Sedimentation Bench Test: Colorado

control | 0 ppm ClO_2 | 60 ppm ClO_2 | 90 ppm ClO_2 | 60 ppm ClO_2 + 40 ppm Na_2SO_4 | 90 ppm ClO_2 + 40 ppm Na_2SO_4

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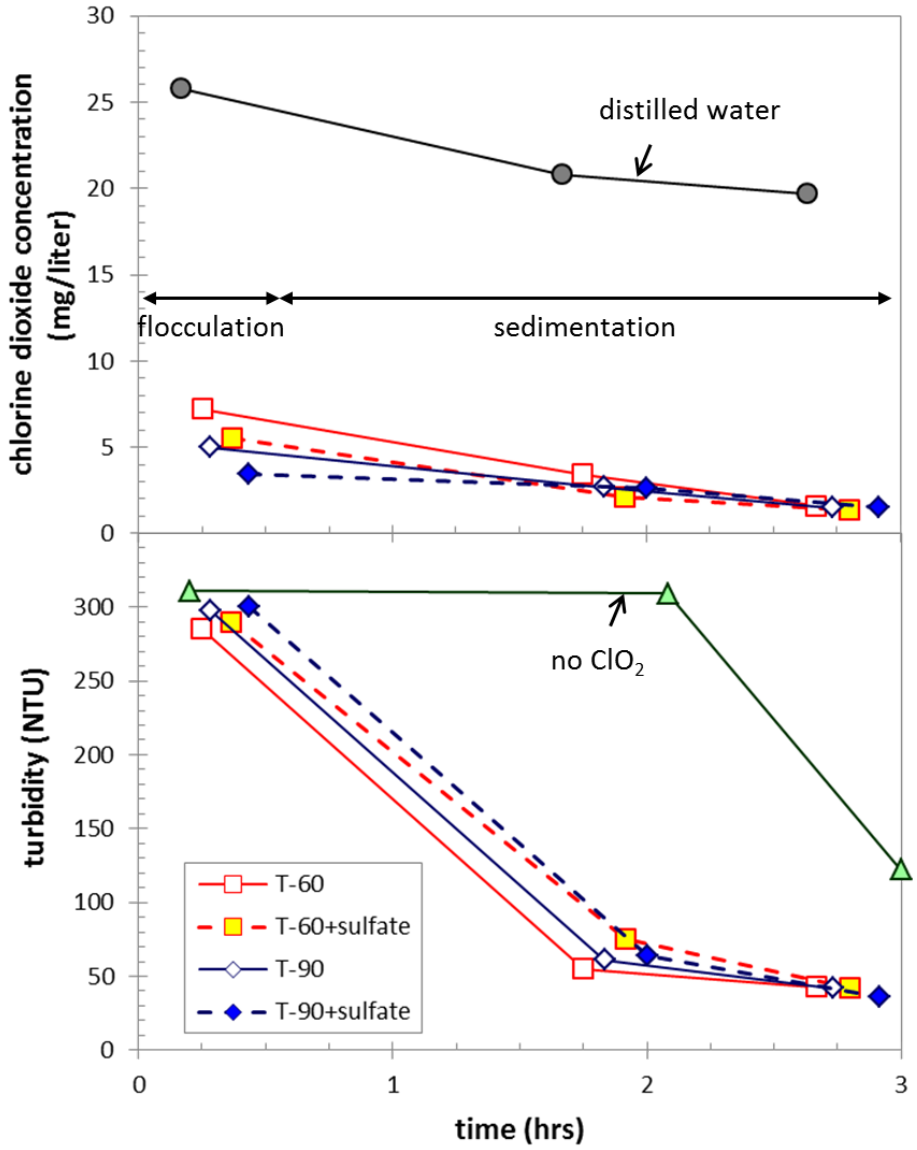
Coagulation-Flocculation-Sedimentation Bench Test Results: Colorado



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Coagulation-Flocculation-Sedimentation Bench Test Results: Colorado

parameter	units	treatment		
		untreated	ClO_2 only	ClO_2 + Na_2SO_4
sodium	mg/liter	7,960	8,340	7,520
potassium	mg/liter	46	36	34
calcium	mg/liter	567	588	551
magnesium	mg/liter	65	67	63
barium	mg/liter	**16**	**16**	**12**
strontium	mg/liter	**109**	**109**	**97**
iron	mg/liter	**65**	**2.8**	**2.8**
manganese	mg/liter	**1.2**	**0.7**	**0.5**
chloride	mg/liter	13,200	10,900	7,860
alkalinity	mg/liter as $CaCO_3$	354	406	399
sulfate	mg/liter	**BDL**	**BDL**	**22**
total sulfides	mg/liter	**10**	**BDL**	**BDL**
total suspended solids	mg/liter	**335**	**42**	**36**
turbidity	NTU	**310**	**42**	**36**
pH		6.4	6.9	6.8
density	mg/liter	1.01	1.01	1.01

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Coagulation-Flocculation-Sedimentation Bench Test: North Dakota

control 0 ppm 10 ppm 20 ppm 40 ppm 80 ppm

before treatment

end of flocculation

settle for 2 hours

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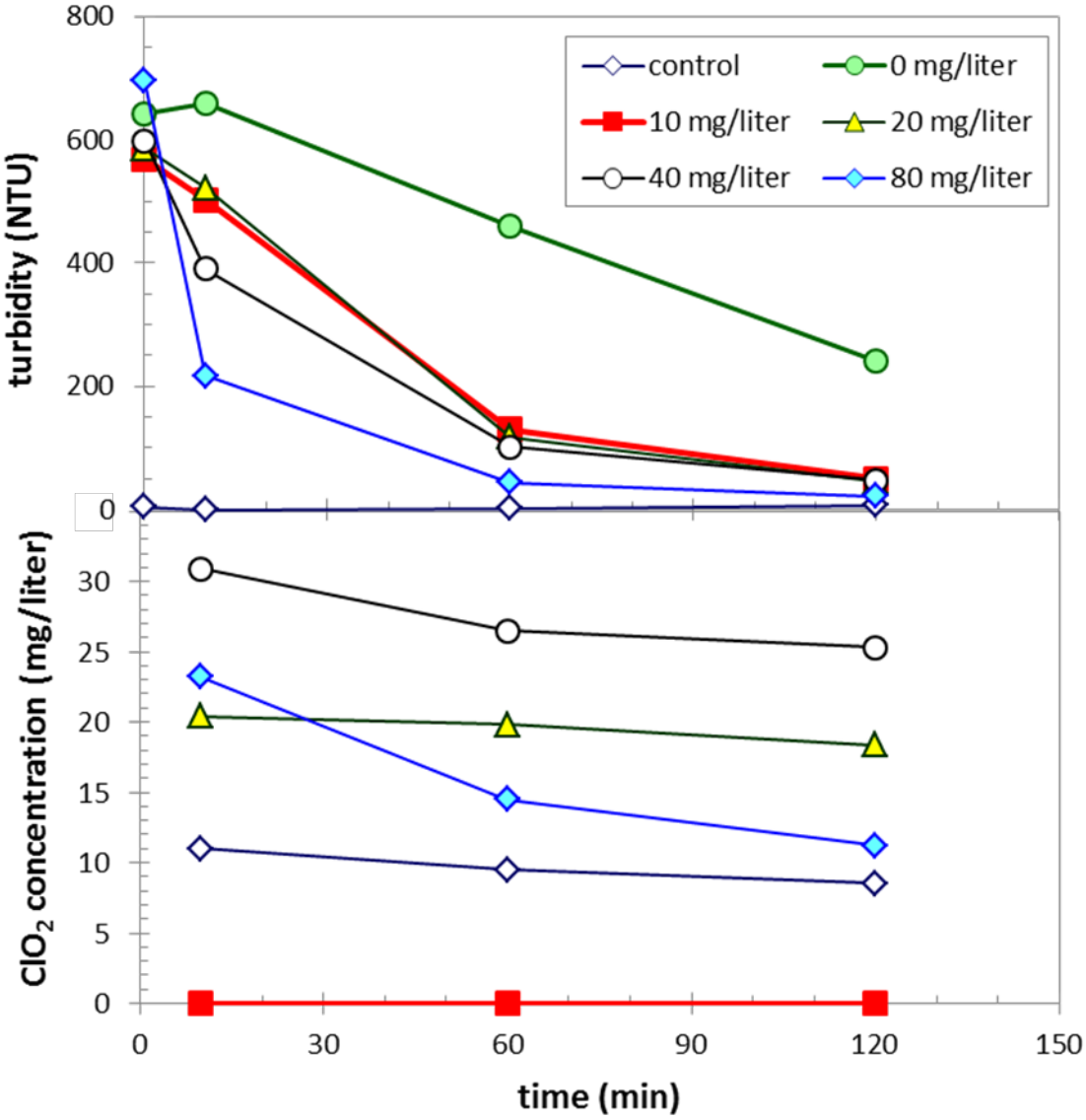
Coagulation-Flocculation-Sedimentation Bench Test Results: ND



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Coagulation-Flocculation-Sedimentation Bench Test Results: ND

parameter	units	treatment	
		no ClO_2	20 mg ClO_2/liter
sodium	mg/liter	74,000	68,600
potassium	mg/liter	5,480	5,570
calcium	mg/liter	17,100	17,000
magnesium	mg/liter	1,430	1,430
barium	mg/liter	11.6	11.5
strontium	mg/liter	1,500	1,450
iron	mg/liter	**24.7**	**2.5**
manganese	mg/liter	16.5	15.8
chloride	mg/liter	162,000	165,000
alkalinity	mg/liter as $CaCO_3$	413	402
sulfate	mg/liter	325	310
total suspended solids	mg/liter	**1,110**	**164**
turbidity	NTU	**240**	**45**
pH		6.9	6.9
density	mg/liter	1.20	1.20

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Estimation of Treatment Costs for Specific Examples

- Costs were estimated for doses of 20 mg/liter, 60 mg/liter, and 230 mg/liter. Average water flow rates ranging from 5,000 to 10,000 bbl/day were considered.
- Cost estimates include all chemical, equipment and labor required for a three year project
- Equipment includes:
  - redundant 3-chemical ClO_2 reactors
  - PCAs for in-line monitoring of ClO_2 residual concentration
  - motive water pumps
  - distribution water pumps
  - ClO_2 snifter
  - bulk chemical storage tanks
  - injection quills
  - communications package for remote monitoring
  - freight and installation
- Sludge removal is not included in example costs

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Treatment Costs for Specific Examples

average water flow rate* (bbl/day)	ClO_2 dose (mg/liter)	treatment cost ($/bbl)
10,000	20	$0.15
10,000	60	$0.23
10,000	230	$0.61
7,000	20	$0.19
7,000	60	$0.28
7,000	230	$0.65
5,000	20	$0.25
5,000	60	$0.33
5,000	230	$0.71

*assumes operation for 350 days/yr

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Conclusions

- Chlorine dioxide is an effective coagulant for removal of suspended solids from produced water and flowback
  - ClO_2 oxidizes dissolved iron (Fe^{2+}) to form solid $Fe(OH)_3$, which acts as coagulant
  - turbidities <10 NTU and suspended solids concentrations <20 mg/liter are achievable
- Treatment with chlorine dioxide will oxidize iron, sulfides (in any form), and kill any bacteria that are present
- Flocculation and sedimentation can remove important scale species, such as barite and calcite
  - this process can be modified to remove scale-causing compounds (e.g., calcium, barium, bicarbonate) that are not present above the saturation limit in the raw water
- Costs for chemicals, equipment, and labor range from $0.15/bbl to $0.71/bbl depending on the flow rate and water quality

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Questions?