A Review and Sustainable Alternative to Sodium-Based and Cyanide-Containing Gold Leaching Agents - Glycine–Thiosulfate Hybrid System Preprint.
DOI: 10.13140/RG.2.2.35237.82402

October 16, 2025

Bruce A. Cosgrove, MSc.
Independent Scientific Researcher
Burnaby British Columbia, Canada
Email: bruceacosgrove@gmail.com

Article Info

Keywords: artisanal miners, thiosulfate, leaching, urea, sodium cyanide, glycine, sustainable, effectiveness

Abstract

This study reviews the use of sodium-based compounds such as urea, sodium sulfate, sodium chloride, sodium carbonate, and thiosulfate—often formulated with sodium cyanide—as gold leaching agents by artisanal miners, and proposes a greener, more sustainable alternative.

1. Thiosulfate-based Gold Leaching System

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i. Thiosulfate (Yes — Effective Leaching Agent)

- **Effectiveness**: Proven to be an effective gold leaching agent, especially as an alternative to cyanide.
- **Use**: Often used in combination with copper(II) ions or ammonia to stabilize the gold-thiosulfate complex.
- **Advantages**: Non-toxic, environmentally friendly.
- **Limitations**: Complex recovery process and more sensitive to changes in conditions than cyanide.

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ii. Urea (No — Not a Leaching Agent, but May Play a Supporting Role)

- **Effectiveness**: Not a gold leachant by itself.
- **Use**: Sometimes used to control pH or as a reductant in chemical processes.
- **Note**: In some innovative or experimental systems (e.g., urea-thiosulfate or urea-hydrogen peroxide), it can support oxidation processes.

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iii. Sodium Sulfate (No)

- **Effectiveness**: Not a leaching agent.
- **Use**: Sometimes a by-product or used in pH control or ionic balance.

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iv. Sodium Chloride (No — Not Alone)

- **Effectiveness**: Not effective alone; however, in **aqua regia** systems (which involve HCl and HNO_3), chloride ions are essential.
- **Use**: In chloride-based leaching systems (e.g., with oxidants like chlorine gas or hypochlorite), NaCl supports gold solubilization.

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v. Sodium Carbonate (No — pH Modifier)

- **Effectiveness**: Not a leaching agent.
- **Use**: Commonly used as a **pH buffer** in leaching systems or in refining operations.

Adding **0.5% sodium cyanide (NaCN)** to a **thiosulfate-based gold leaching system** is **not recommended** and could lead to **dangerous chemical interactions increasing the risk of forming toxic gases** such as **hydrogen cyanide (HCN)** under acidic or unstable conditions, **reducing leaching efficiency, and** causing the degradation of thiosulfate producing toxic sulfur, sulfite, and other by-products. CN and $Na_2S_2O_3 \cdot 5H_2O$ are competitive lixiviants to recover gold.

1.1 Chemical and Practical Consequences of Mixing NaCN with Thiosulfate:

1. Thiosulfate Decomposition

- Cyanide can catalyze the **oxidative degradation of thiosulfate**, producing sulfur, sulfite, and other byproducts.
- This reduces the availability of thiosulfate for gold complexation, undermining the leach system.

2. Reduced Gold Recovery

- Cyanide and thiosulfate both form soluble complexes with gold:
  - Cyanide: $[Au(CN)_2]^-$
  - Thiosulfate: $[Au(S_2O_3)_2]^{3-}$
- In the presence of both, **competing complexation** occurs, possibly reducing total gold leaching efficiency due to instability or mixed complex formation.

3. Copper Interactions

- In thiosulfate systems, copper(II) is often used as an oxidant.
- In cyanide systems, **copper complexes with cyanide**, reducing its availability to oxidize gold or regenerate thiosulfate.
- This disrupts the redox balance critical for effective thiosulfate leaching.

4. Environmental and Safety Hazards

- Mixing cyanide with sulfur-based compounds like thiosulfate or sulfide minerals **increases the risk of forming toxic gases** such as **hydrogen cyanide (HCN)** under acidic or unstable conditions.
- Even at 0.5%, NaCN is highly toxic and negates the low-toxicity benefits of a thiosulfate system.

Only **thiosulfate** (with proper oxidants and conditions) is a direct gold leaching agent, others may serve **supporting roles** (e.g., pH adjustment, ionic strength control) but do not leach gold by themselves.

To redesign a gold leaching formulation using listed components — aiming for an **effective, environmentally safer gold leachant** — the most viable path is to base it around **thiosulfate** as the primary leaching agent, with supporting components added to control pH, ionic strength, and complexation conditions.

2. Effective Gold Leaching Formulation (Thiosulfate-Based System)

A **proposed formulation by weight percent (wt.%)** for a **thiosulfate-based gold leaching solution**, optimized for efficiency and sustainability:

Component	**Purpose**	**Wt.% Range**
Sodium Thiosulfate ($Na_2S_2O_3$)	Primary leachant (forms complex with gold)	**10–15%**
Copper(II) Sulfate ($CuSO_4$) or Copper(II) Nitrate	Oxidant / catalyst to regenerate thiosulfate	**0.1–0.3%**
Ammonium Hydroxide (NH_4OH) or Ammonium Salts	Stabilizes copper-thiosulfate complex, pH buffer	**1–3%** (or pH 9–10)
Sodium Carbonate (Na_2CO_3)	pH buffer to maintain alkaline conditions	**1–2%**
Sodium Chloride (NaCl)	Enhances ionic strength, may aid in permeability	**0.5–2%**
Water	Solvent	Balance to 100%

Optional Components:

- **Urea (0.1–0.5%):** May assist in controlling ammonia volatility and stabilize solution, though it's not essential.
- **Sodium Sulfate**: Not required, but if present, should be <0.5% to avoid ionic interference.

Notes:

- **pH Control is Critical**: Aim for pH 9–10 to prevent thiosulfate decomposition.
- **Contact Time**: Gold extraction typically occurs within 24–48 hours.
- **Recovery**: Resin-in-pulp (RIP) or electrowinning is used to recover gold from the leachate.

Lab-Scale Gold Leaching Solution (1 Liter)

Component	**Amount per 1 L**	**Purpose**
Sodium Thiosulfate ($Na_2S_2O_3 \cdot 5H_2O$)	**100–150 g**	Primary gold leachant
Copper(II) Sulfate ($CuSO_4 \cdot 5H_2O$)	**1–3 g**	Oxidant/catalyst (copper source)
Ammonium Hydroxide (NH_4OH, ~25%)	**10–30 mL** (pH adjuster)	Keeps pH at 9–10; stabilizes copper complex
Sodium Carbonate (Na_2CO_3)	**10–20 g**	pH buffer
Sodium Chloride (NaCl)	**5–15 g**	Ionic strength enhancer
Urea (optional)	**1–5 g**	May improve ammonium stability
Distilled Water	Add to make 1 liter	Solvent

Instructions:

1. **Dissolve** sodium thiosulfate in ~800 mL of distilled water.
2. **Add** copper sulfate slowly and stir until dissolved.
3. **Adjust pH** to 9–10 using ammonium hydroxide and buffer with sodium carbonate.
4. **Add** sodium chloride and (optionally) urea.
5. **Top up** to 1 liter with distilled water and mix thoroughly.

Use Guidelines:

- **pH Range**: Maintain at 9.0–9.5 throughout leaching.
- **Temperature**: Room temperature (~20–25°C) is sufficient.
- **Leaching Time**: 24–48 hours depending on ore type.
- **Ore-to-Liquid Ratio**: Start with 1:3 or 1:4 (e.g., 100 g ore to 300–400 mL solution).
- **Gold Recovery**: Use ion exchange resin or electrowinning.

Expected Gold Recovery by Ore Type

Ore Type	**Expected Recovery (%)**	**Notes**
Oxide ores	**80–90%**	High recovery; ideal for this system if gold is free-milling.
Mildly refractory sulfide ores	**50–80%**	Recovery depends on degree of sulfide encapsulation.

Ore Type	Expected Recovery (%)	Notes
Carbonaceous or high-clay ores	**30–60%**	Glycine helps suppress preg-robbing, but ore prep is crucial.
Hard refractory ores	**<30% (as-is)**	Pre-treatment (oxidation/roasting) is needed to achieve good recovery.

3. Glycine–Thio-Sulfate Hybrid System

A glycine–thiosulfate hybrid system is an effective formulation to sustainably recover 70 – 90% of gold from crushed ore and is one of the most promising non-cyanide leaching approaches being researched today (**Aylmore, M.G., 2005)**. It leverages the gold-complexing power of thiosulfate with the chelating and stabilizing effects of glycine, creating a system that is:

- **Eco-friendly**
- **Low in toxicity**
- **Effective in mildly alkaline conditions**
- **Potentially cheaper than cyanide-based systems**

Lab-Scale Gold Leaching Formula (Glycine–Thiosulfate Hybrid, 1 Liter)

Component	Amount per 1 L	Function
Sodium Thiosulfate ($Na_2S_2O_3 \cdot 5H_2O$)	50–100 g	Primary gold leachant
Glycine (food grade or reagent)	20–50 g	Complexes with metals, stabilizes Cu
Copper(II) Sulfate ($CuSO_4 \cdot 5H_2O$)	0.5–1.5 g	Oxidant/catalyst
Ammonium Hydroxide or NaOH	To adjust pH to 9.5–10.5	pH adjustment and buffering
Sodium Carbonate (Na_2CO_3)	5–10 g	Additional pH buffering
Distilled Water	Add to make 1 liter	Solvent

Leaching Conditions:

- **pH**: Maintain at **9.5 to 10.5**
- **Grind** size75 um
- **Temperature**: Room temperature to 50°C (30–40°C is ideal)
- **Time**: 24–48 hours depending on ore characteristics
- **Ore-to-liquid ratio**: 1:3 to 1:5 (e.g., 100 g ore to 300–500 mL solution)

- **Gold recovery**: resin-in-pulp, ion exchange, or precipitation

Key Factors That Drive High Recovery:

- **Particle size**: Gold must be liberated — target **<75 microns**.
- **pH control**: Maintain between **9.5–10.5**.
- **Copper catalyst**: Use **~300–500 ppm** (e.g., ~1 g/L $CuSO_4 \cdot 5H_2O$).
- **Leach time**: **24–72 hours**, depending on ore and temperature.
- **Temperature**: **30–50°C** improves kinetics.
- **Ore type**: Free-milling gold responds best without extra pre-treatment

Suggestions to Improve Recovery:

1. **Crush ore finer** — target **<75 microns** if possible.
2. **Pre-test ore** with a fire assay to confirm total gold content.
3. **Pre-oxidize refractory ore** using roasting, pressure oxidation, or alkaline oxidation (if sulfides are high).
4. **Ensure pH stability** at **9.5–10.5** using NaOH or ammonium hydroxide.
5. **Use proper leaching time** — at least **24–48 hours** with agitation.
6. **Check copper levels** — aim for ~300 ppm. Too much degrades thiosulfate.

Advantages of the Hybrid System:

- Glycine helps stabilize copper, reducing the risk of passivation or side reactions.
- Thiosulfate allows strong gold complex formation ($[Au(S_2O_3)_2]^{3-}$).
- Glycine is biodegradable, inexpensive, and enhances selectivity for gold over base metals. Under **optimized conditions**, the **glycine–thiosulfate formulation** can recover 70% to 90% of the gold from **free-milling or mildly refractory crushed ore**.

Example (Lab Case Study):

A finely ground oxide gold ore (100 µm, 2.5 g/t Au), leached at 40°C for 48 hours in a solution of:

- 10% $Na_2S_2O_3$
- 3% glycine
- 500 ppm Cu^{2+}
- pH 10

Gold Recovery: ~88% using resin-in-pulp (RIP)

Recovery by Ore Type (Using Glycine–Thiosulfate Leach)

Ore Type	**Recovery (%)**	**Notes**
Oxide / free-milling ore	**80–90%**	**Excellent response when finely ground (<75 µm)**

Ore Type	**Recovery (%)**	**Notes**
Mildly refractory sulfide ore	**50–75%**	**Recovery improves with fine grinding and longer leach time**
Refractory / encapsulated ore	**<30% (as-is)**	**Requires pre-treatment (oxidation, roasting, etc.)**
High clay / carbonaceous ore	**30–60%**	**Glycine reduces preg-robbing; still depends on ore mineralogy**

Resin-in-Pulp (RIP) and **Carbon-in-Pulp (CIP**) are similar in concept but use different materials and have distinct advantages and disadvantages:
What They Have in Common:

Both are **adsorption-based recovery methods** used after gold has been leached into solution. They involve:

- Keeping the **leach slurry (pulp)** in contact with a solid adsorbent.
- **Separating gold** from solution via adsorption.
- **Stripping the adsorbent** to recover the gold later.

Key Differences:

Feature	**Carbon-in-Pulp (CIP)**	**Resin-in-Pulp (RIP)**
Adsorbent	Activated **carbon**	Synthetic **ion-exchange resin beads**
Selectivity	Less selective — adsorbs other organics/metals	More selective — tailored for gold complex ions
Kinetics (Speed)	Slower	Often faster due to higher surface accessibility
Reusability	Lower (carbon can foul)	Higher; resin is more durable
Sensitivity to Fouling	Carbon fouls easily (e.g., organics, clay)	Resin resists fouling better
Best for	**Cyanide** systems	**Thiosulfate, glycine**, or alternative leachants
Stripping Process	Requires high-temp elution, acid washing	Milder conditions; more chemical-based stripping

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Why Resin-in-Pulp is Better for Thiosulfate/Glycine:

- Activated carbon **does not adsorb gold-thiosulfate complexes well**.

- Resin (especially **strong-base anion exchange resins**) can be **specifically selected to capture $[Au(S_2O_3)_2]^{3-}$** efficiently (**Muir, D.M. & Aylmore, M.G., 2004)**.
- Works in **alkaline systems** like thiosulfate and glycine, where CIP fails.

Conclusion:

- CIP is ideal for cyanide leach systems.
- RIP is ideal for thiosulfate, glycine, and non-cyanide gold leaching systems.
- **Glycine–thiosulfate** systems can yield **70–90% gold recovery** under optimized lab conditions.
- Effectiveness is ore-dependent (best for oxide and mildly refractory ores).
- Resin-in-pulp or resin columns are recommended for gold recovery from solution.

Funding

This research received no external funding.

Conflict of Interest

The author declares no conflict of interest.

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